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Midwest Research Inst.
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EVALUATION OF CHEMICAL AGENTS FOR INHIBITING ACID MINE DRAINAGE FORMATION

Prepared for

UNITED STATES DEPARTMENT OF THE INTERIOR
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by

Midwest Research Institute
425 Volker Boulevard
Kansas City, Missouri 64110

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Midwest Research Institute
425 Volker Boulevard
Kansas City, [redacted] 64110
MO.

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This report contains findings from a Bureau of Mines study concerning the inhibition of acid mine drainage formation from underground coal mines. A series of experiments was performed in which three different pyritic materials (wastes from coal production plants) were evaluated using several candidate inhibiting agents. Data obtained from the inhibitor-treated pyrites were compared with data from control experiments in which untreated pyritic wastes were used. The experiments were conducted by placing treated and untreated pyrite in columns, passing moist air through the columns to promote oxidation of pyrite, and washing the columns weekly to collect oxidation products for analysis. The results indicate that quantities of acid mine drainage can be substantially reduced if soluble iron III (ferric) ion is controlled.

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John W. Nebgen
Douglas F. Weatherman

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For

U.S. Department of the Interior
U.S. Bureau of Mines
Twin Cities Mining Research Center
P.O. Box 1660
Twin Cities, Minnesota 55111

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FOREWORD

This report was prepared by Midwest Research Institute, Kansas City, Missouri, under USBM Contract No. J0366036. The contract was initiated under the Department of the Interior and Related Agencies Appropriation Act, 1976 (P.L. 94-165, 89 STAT 984), dated December 23, 1975. It was administered under the technical direction of Twin Cities Mining Research Center with Mr. William H. Engelmann acting as Technical Project Officer. Patr k J. Neary was the Contract Administrator for the Bureau of Mines. This eport is a summary of the work recently completed as part of this contract during the period June 25, 1976, to May 24, 1978. This report was submitted by the authors on June 7, 1978.

The principal investigator for the program has been Dr. John W. Nebgen, Senior Advisor for Chemistry. Laboratory work was performed by Mr. Douglas F. Weatherman, Associate Scientist. The authors acknowledge the help and oversight of Dr. A. D. McElroy, Senior Advisor for Applied Sciences. Questions concerning this report should be directed to Dr. Nebgen.

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EVALUATION OF CHEMICAL AGENTS FOR INHIBITING ACID MINE DRAINAGE FORMATION

by

J. W. Nebgen and D. F. Weatherman

ABSTRACT

This report contains findings from a U.S. Bureau of Mines study concerning the inhibition of acid mine drainage formation from underground coal mines. A series of experiments was performed in which three different pyritic materials (wastes from coal production plants) were evaluated using several candidate inhibiting agents. Data obtained from the inhibitor-treated pyrites were compared with data from control experiments in which untreated pyritic wastes were used. The experiments were conducted by placing treated and untreated pyrite in columns, passing moist air through the columns to promote oxidation of pyrite, and washing the columns weekly to collect oxidation products for analysis.

Experimental results indicate that quantities of acid mine drainage can be substantially reduced if soluble iron III (ferric) ion is controlled. The best inhibitors are neutral or alkaline siliceous materials such as fly ash, blast furnace slag, portland cement, and cement kiln dust. These materials appear to insolubilize iron III species to make them unavailable for reaction with pyrite. The data strongly suggest that the soluble ferric ion aqueous is a key oxidant for pyrite to produce acid mine drainage. The role of aqueous ferric ion as an oxidizing agent is substantiated further by data obtained using metallic iron (nails) as an inhibitor. The iron nails tended to keep the soluble iron in the iron II (ferrous) state. Experimental results indicate that sulfate and acidity levels are reduced when pyrite is in contact with the metallic iron.

INTRODUCTION

This report describes a study in which chemical materials were evaluated to prevent or inhibit formation of acid mine drainage from underground coal mines. Acid mine drainage from underground coal mines arises from the oxidation of pyritic residues in exposed faces and rubble to form iron sulfates and sulfuric acid. In many cases, these faces are wet with a thin film of water which carries the reaction products into a pool or reservoir. When the reservoir fills to capacity, the acidic products from the pyrite oxidation can find their way to surface waters where they can drop stream pH to levels detrimental to stream biota, and can precipitate iron salts in the form of "yellow-boy," a slimy material consisting of ferric hydroxide found in many streams in coal mining regions.

The purpose of the study was to evaluate various chemicals to determine whether pyrite oxidation on the pyritic surfaces inside the mine could be inhibited. We have found that oxidation can be controlled if pyritic surfaces are coated with materials which are both alkaline and siliceous such as fly ash, blast furnace slag, portland cement, or cement kiln dust. We have found further that pyrite oxidation can occur if an agent with greater reducing potential than pyrite is present in the system. The agent most carefully evaluated in the study was metallic iron. Inhibition in this case consisted of providing a material with which oxygen could react more readily than it could with pyrite.

Experiments were conducted by mixing pyrite with candidate inhibition agents in several columns. Moist air was passed through the columns to promote pyrite oxidation. Reaction products from the pyrite were collected weekly by washing the material in the column with distilled water. The collected leachates were analyzed for ferrous iron (iron II), total iron, sulfate, acidity and alkalinity, and pH. Results from experiments in which pyrite was mixed with inhibiting agents were then compared to the results obtained from a control experiment involving a non-inhibited pyrite.

Three pyrites were evaluated in some depth. The materials used were pyritic wastes from coal preparation plants. Only one of the three was acid-producing. Thus, we reaffirmed the long-standing observation that many pyrite wastes do not have acid mine drainage problems. Evaluation of these wastes showed further that the one acid producer was associated with bacterial colonies of thiobacillus, whereas bacterial colonies could not be established in the other two. Thus, our observations are consistent with those of many other researchers who have noted the important role of bacteria in accelerating the formation of acid mine drainage.

The principal mechanism for controlling acid mine drainage formation at the source, however, is not by control of bacteria. Rather, it appears to be control of ferric ion concentrations in aqueous solution. If ferric ion can be minimized by preventing oxidation of aqueous ferrous ion, then the quantity of pyritic oxidation products in mine drainage can be substantially reduced. One method of controlling soluble ferric ion is to provide a reducing agent stronger than pyrite to act as a sacrificial electrode. This study shows that metallic iron is such a reducing agent. A second method of controlling ferric ion concentrations is the immobilization of ferric ion (and perhaps ferrous ion) in a silicate matrix. This mechanism is believed to be the more effective control, since it simply removes any soluble iron oxidation products from the system so that soluble ferric ion cannot be present for pyrite oxidation.

In the following sections of this report, we will describe the experimental procedures used and discuss the experimental results obtained. The experimental results have been analyzed by statistical methods to establish confidence limits of the experimental data. We shall also discuss in some detail mechanisms for inhibition of acid mine drainage formation. The report concludes with our conclusions and recommendations. Raw data from the experiments are attached as appendices to the report.

PYRITE CHARACTERIZATION

The purpose of this study was to determine whether acid mine drainage formation could be inhibited by chemical means. Thus, we undertook to evaluate a number of pyrites with varying degrees of potential for acid generation so that the effects of candidate inhibitors could be clearly seen and measured. Six different pyritic materials were evaluated during the program obtained from four sources.

* Robena - pyritic waste from U.S. Steel's Robena Coal Preparation Plant near Greensboro, Pennsylvania.

* Maple Creek - pyritic waste from U.S. Steel's Maple Creek Coal Preparation Plant at New Eagle, Pennsylvania.

* Valley Camp Nos. 1 and 3 - pyritic waste from two coals mined by the Valley Camp Coal Company, Trialdelphia, West Virginia.

* Kraft Coarse (+200 mesh) and Intermediate (-200 mesh) - commercial grade pyrites supplied by the Kraft Chemical Company, Chicago, Illinois.

The two Kraft pyrites are relatively pure. A typical analysis supplied with the pyrite indicates an iron content of 45.68%, a sulfur content of 52.09%, and silica content of 0.88%. The remaining 1.35% has not been accounted for.

The other four pyritic materials are derived from coal preparation operations, and consist of pyrite intermixed with shale and finely divided coal. Attempts to analyze these materials were unsuccessful because of the intimate mixture. Even under rigorous digestion in hot nitric acid, we were unable to separate the sulfur and iron components of pyrite from the coal/shale matrix. Similarly, the coal fraction could not be readily separated from the heavier shale and pyrite components of the materials.

The coal-derived pyritic materials were subjected to a sieve analysis to determine particle size distribution. Results of the sieve analysis are presented in Figure 1 along with that reported for the Kraft Coarse pure pyrite. The Kraft Intermediate pyrite was very finely divided (-200 mesh) and not subjected to further sieve analysis. As can be seen from the figure, the coal-derived pyrite is much coarser than the commercial pyrite.

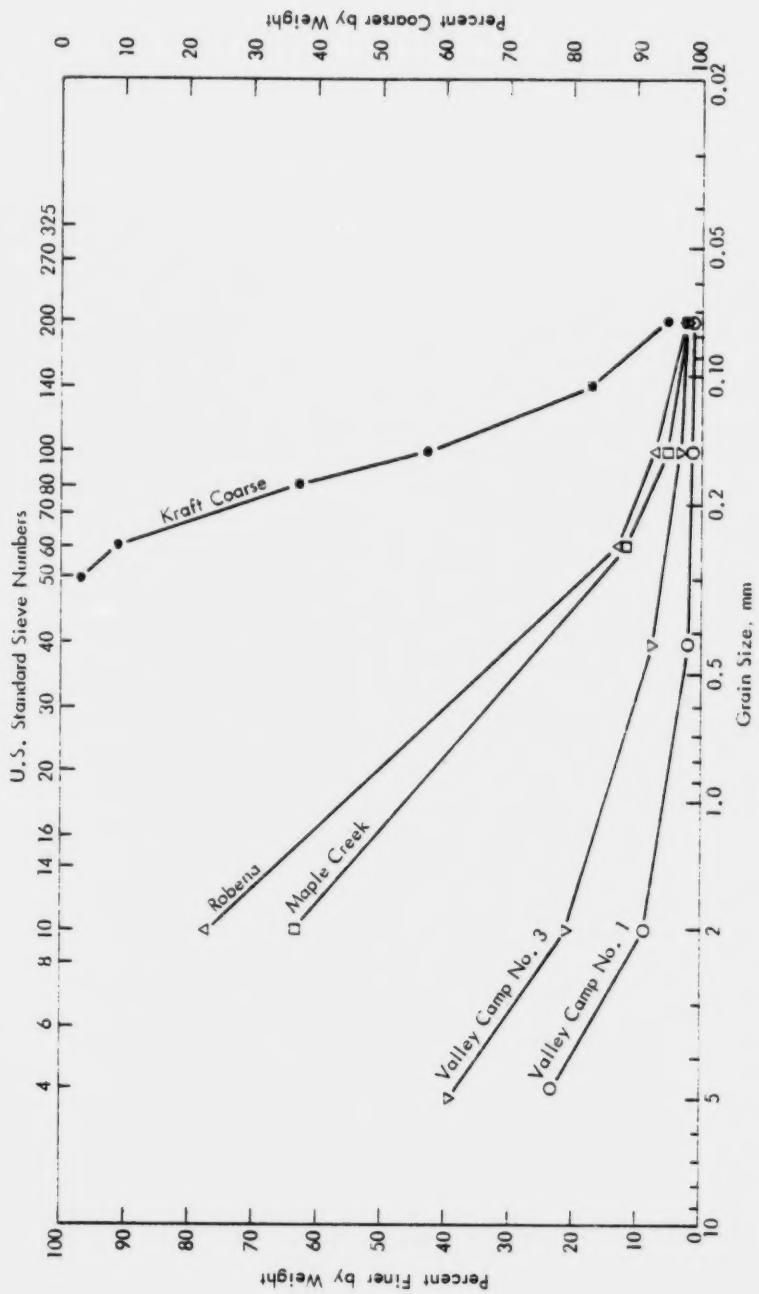


FIGURE 1. - Particle size distribution of pyrites used in the experiments.

The oxygen uptake rates of the six pyrites were determined by placing 5 g of the material bottles containing 157 ml of distilled water. The bottles (500-ml capacity) were placed on a Hach Chemical Company Biological Oxygen Demand (BOD) Apparatus and pressure drops due to oxygen consumption were measured. The bottle caps are connected individually to mercury manometers. As air trapped in the sealed bottles is consumed, a partial vacuum is created in the bottle which can be measured on the manometer. The samples are continuously stirred while on the apparatus to promote oxidation. By following the amount of vacuum developed as a function of time, it is possible to determine the amount of oxygen consumed as a function of time. The reaction of oxygen with pyrite is strictly chemical, since the water was not seeded with Thiobacillus.

The results of the oxygen uptake experiments are plotted in Figure 2 (Robena and Maple Creek), Figure 3 (Valley Camp Nos. 1 and 3), and Figure 4 (Kraft Coarse and Intermediate). From these plots, it is seen that the rate of oxygen uptake is proportional to particle size. The slowest rates were observed with the two Valley Camp pyrites, whereas the fastest were seen with the Kraft pyrites.

The Valley Camp No. 1 pyrite was observed to be the slowest in the week-long oxygen uptake experiment. We observed no pressure drop during the first 3 days, and then pressure dropped slowly. A lag time of 1 day was also noted in the Valley Camp No. 3 and the two commercial grade pyrites. As was discovered later in the program, Valley Camp No. 1 pyrite turned out to be the most consistent acid producer. Robena and Maple Creek pyrites, which consumed oxygen in the initial experiments, could not be made to produce acid mine drainage in great quantity. Thus, formation of acid mine drainage by pyrite oxidation appears to require a period of acclimation before oxygen/pyrite reaction becomes rapid, and, hence, short-term oxygen uptake experiments do not necessarily reflect the tendency of a particular pyrite towards acid mine drainage formation.

The fastest oxygen uptake was observed with the Kraft Intermediate material, about 4.3 mg O_2 per gram pyrite over a 7-day period. Morth et al. (1) report an oxygen uptake rate of 25 μg O_2 per hour in air at 25°C for a 1-g sample of 60 mesh (650 μm) concentrated pyrite material. This rate extrapolated to 7 days is 4.2 mg O_2 per gram. However, these particle sizes of the Kraft Intermediate pyrite is less than 200 mesh (74 μm) as it appears that oxygen uptake rates we observed are somewhat slower than those observed by Morth et al. The difference in oxygen consumption rates may be due to the fact that our experiments depended upon diffusion of gaseous oxygen through about 3 cm of liquid water to reach the pyrite.

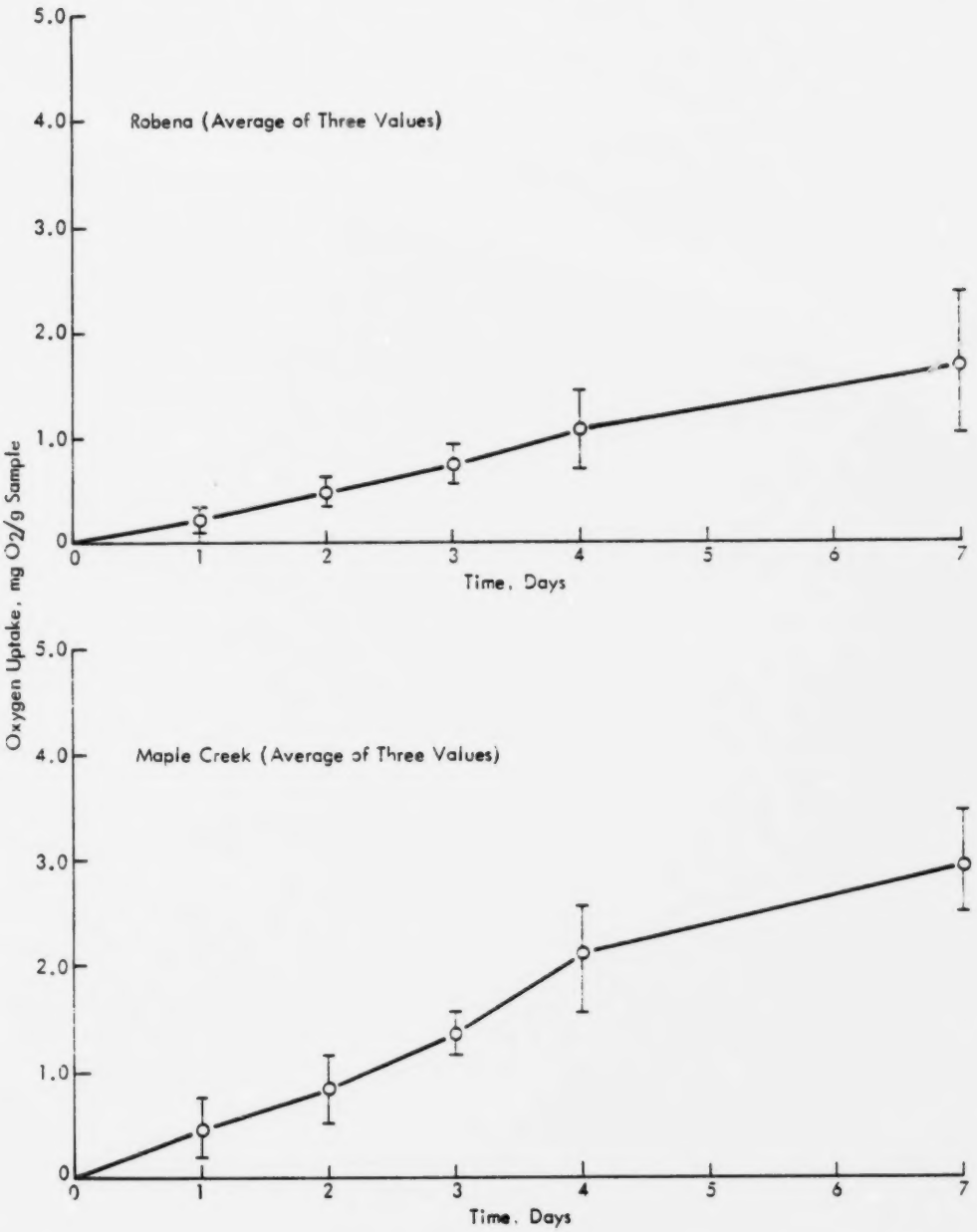


FIGURE 2. - Oxygen uptake rates: Robena and Maple Creek pyrites.

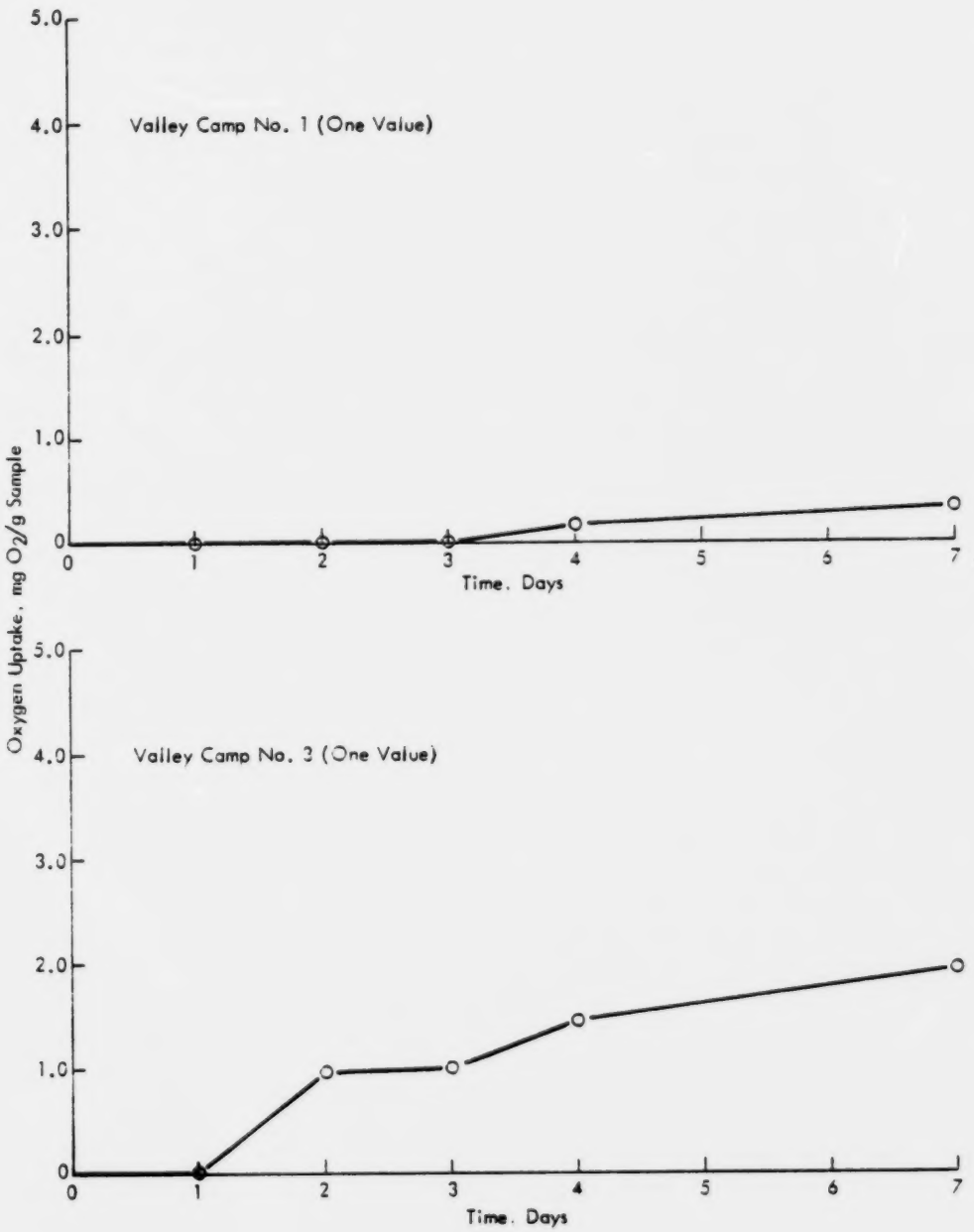


FIGURE 3. - Oxygen uptake rates: Valley Camp Nos. 1 and 3 pyrites.

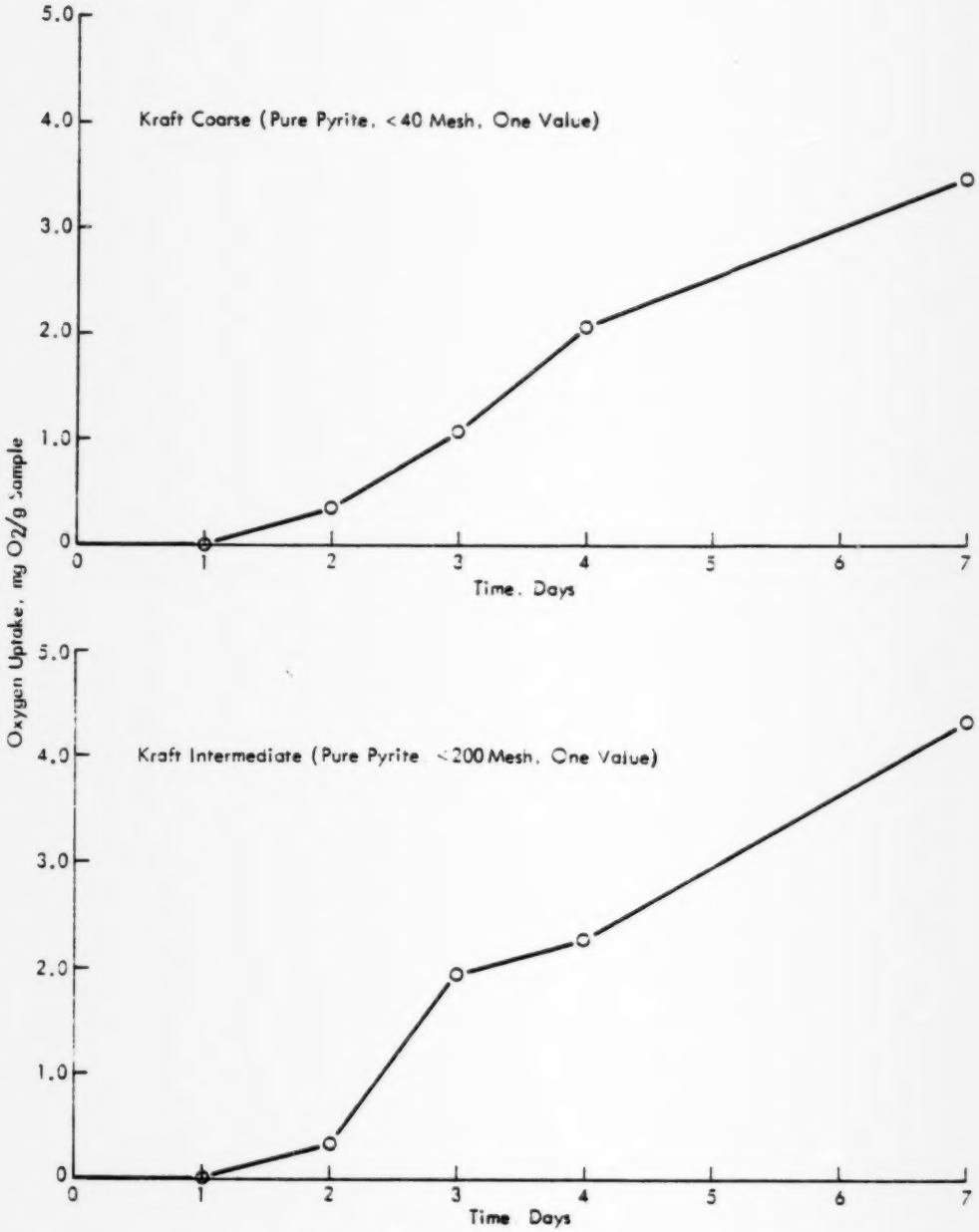


FIGURE 4. - Oxygen uptake rates: Kraft Coarse and Intermediate pyrites.

After the 7 days of oxygen uptake, the composition of the aqueous phase of the system was determined. Constituents sought were:

* Iron II (ferrous),

* Iron total,

* Sulfate ($SO_4^{=}$),

* Acidity and alkalinity, and

* pH.

The two types of iron were determined using colorimetric procedures involving the formation of a red complex with 1,10-phenanthroline. Powder pillows supplied by the Hach Chemical Company, Ames, Iowa, were used to develop the color, the intensity of which was measured on a Hach Chemical Company DR-EL/2 spectrophotometer. Hach's proprietary ferrous iron powder pillows were used for the iron (II) determinations and their FerroVer powder pillows for total iron. Ferric iron in solution then is the difference between total iron and ferrous iron.

Sulfate was determined spectrophotometrically also using Hach Chemical Company methods. This method involved the addition of a SulfaVer IV powder pillow to a 25-ml sample and resulting turbidity measured on the DR-EL spectrophotometer.

Acidity and alkalinity were determined by titrating samples with standard base and acid. Samples were titrated with 0.02 N sodium hydroxide to the phenolphthalein end point for acidity (pH = 8.3), and with 0.02 N hydrochloric acid to the methyl orange end point for alkalinity (pH = 4.5).

The pH was determined using a Beckman Model N pH meter.

In addition to analyzing the aqueous phase from the oxygen uptake experiments, we also washed 5 g of the as-received pyrite in 157 ml of distilled water to determine the amounts of soluble reaction products in the pyrite. This analysis was done in order to establish the degree to which reaction products were increased by oxygen in the uptake experiments.

The results of these two sets of analyses are presented in Table 1. The raw data have been translated from milligrams per liter to milligrams per gram sample. The designation "before reaction" refers to results

TABLE 1. - Soluble constituents in as-received pyrite and after 7-days oxygen uptake

	Robena*	Maple Creek*	Valley Camp No. 1	Valley Camp No. 3	Kraft Coarse	Kraft Inter-mediate
Iron (II), mg/g						
Before reaction	0.0002	0.0002	0.057	0.0009	0.061	0.60
After reaction	0.0004	0.0005	0.0006	0.00	0.0003	0.60
Iron, total, mg/g						
Before reaction	0.0011	0.0005	0.059	0.0041	0.061	0.60
After reaction	0.0010	0.0010	0.0038	0.0072	0.0038	0.60
Sulfate, mg/g						
Before reaction	1.41	0.97	4.24	2.36	1.48	23.6
After reaction	3.71	4.99	5.21	4.40	6.28	30.8
Acidity, mg $CaCO_3$/g						
Before reaction	0.10	0.10	0.82	0.13	0.94	22.7
After reaction	0.13	0.16	0.13	0.25	0.25	19.7
Alkalinity, mg $CaCO_3$/g						
Before reaction	0.77	0.94	0.13	0.69	0.28	0.00
After reaction	0.73	0.93	0.44	0.88	0.47	0.00
pH						
Before reaction	6.3	6.7	4.8	6.6	5.2	2.9
After reaction	6.6	6.9	6.3	6.5	7.6	3.8
Oxygen uptake, mg O_2/g	1.67	2.96	0.32	1.98	3.52	4.32
Net sulfate, mg SO_4/g	2.30	4.02	0.97	2.04	4.80	7.2

* Average of three values.

obtained when the as-received pyrite was washed in distilled water, and "after reaction" refers to composition after 7 days of oxygen uptake in the Hach BOD Apparatus. Included in the table are the oxygen values observed after 7 days shown in Figures 2 through 4.

Analysis of the before reaction and after reaction data indicate that only sulfate is increased by the reaction of oxygen. Iron concentrations (both ferrous and total) are quite small in both the before and after samples. Small quantities of acidity are generated by the Robena, Maple Creek, and Valley Camp No. 3 pyrites, but acidity was consumed in the Valley Camp No. 1, Kraft Intermediate, and Kraft Coarse pyrites. Consumption of acidity is associated with increase in alkalinity. The pH in most systems tended to increase, i.e., systems tended to become less acid, during the oxygen uptake experiments. Thus, on the basis of this analysis, it was concluded that sulfate is the key indicator of pyrite reaction with oxygen.

The relationship between oxygen and sulfate was subjected to a regression analysis. The resulting regression equation is:

$$\text{mg } SO_4/g = -0.181 + 1.518 \text{ (mg } O_2/g)$$

The correlation coefficient for the equation is 0.961, and the standard deviation of the oxygen coefficient is 0.218. The confidence limit of the correlation is between 99 and 99.9%.

Theoretically, 1 mg of oxygen (as O_2) will generate 1.71 mg of sulfate in the oxidation of pyrite from the reaction:

$$FeS_2 + 7/2\ O_2 + H_2O \longrightarrow FeSO_4 + H_2SO_4$$

From the regression equation, based on experimental observations, 1 mg of O_2 would generate 1.34 g sulfate, about 78% of theoretical. Thus, some oxygen is being consumed other than by pyrite sulfur. The very low concentration of soluble iron in the aqueous phase suggests that the 22% excess oxygen is consumed in the oxidation of insoluble ferric iron species. Alternatively, some of the sulfate generated by pyritic sulfur reaction with oxygen might be insolubilized as a basic iron sulfate.

Despite the fact that all of the oxygen consumed by the pyrite cannot be accounted for as sulfate, it is clear that the correlation between oxygen consumption and soluble sulfate formation is very good. For this reason, we have chosen sulfate to be the primary indicator of acid mine drainage formation, e.g., oxygen reaction with pyrite. In subsequent

experiments described in this report, the quantity of sulfate in solutions obtained when columns containing pyrite were flushed with water has been interpreted in terms of chemical inhibition. A small amount of sulfate thus indicates that pyrite/oxygen reactions have been inhibited, whereas a larger quantity of sulfate indicates the opposite.

This characterization of pyrite materials thus provided the basis for the subsequent evaluation of chemical inhibition of acid mine drainage formation.

EXPERIMENTAL PROCEDURES FOR DETERMINING INHIBITION OF ACID MINE DRAINAGE FORMATION

The oxygen uptake experiments described above are useful in establishing the chemical characteristics of pyrite/oxygen reactions. However, they are not representative of acid mine drainage formation in real systems. In real systems involving underground coal mines, acid mine drainage is the result of the flushing away of pyrite oxidation products formed by the reaction of the pyrite by air in the presence of water vapor or a very thin film of liquid water. If liquid water is more than a few micrometers deep, oxidation of pyrite is slowed markedly, since the reaction kinetics become dependent upon diffusion of gaseous oxygen through the water. Therefore, the following procedures were initiated to simulate more realistically acid-forming conditions in an underground coal mine.

The experimental procedure used throughout the program consisted of placing pyrite in columns and passing moist air through the pyrite in an upward direction to promote the formation of acid mine drainage reaction products. Two types of columns were used in the program: small columns for initial screening experiments and large ones for long-term inhibition experiments. The reaction products were flushed from the pyrite at weekly intervals and analyzed for pyrite oxidation products using procedures described in the preceding section. Constituents determined were:

* Iron II,
* Iron total,
* Sulfate,
* Acidity and alkalinity, and
* pH.

Each set of experiments consisted of several different columns exposed to identical conditions of air flow, humidity, and temperature. These results obtained from individual columns could be compared directly to one another to establish differences in pyrite reactivity, degree of reaction inhibition, etc.

Initial Experiments With Small Columns

The initial experiments concerning inhibition were conducted using small columns (1.3 cm diameter by 10 cm long). These experiments were undertaken to ascertain which pyrites had a tendency towards formation of acid mine drainage and to screen candidate agents for the inhibition of pyrite/air/water reactions. Results from these initial experiments are presented in Appendix A.

The results of the pyrite reactivity tests done in the small columns indicated that the Valley Camp No. 1 pyrite was the most reactive in terms of sulfate generated when exposed to the moist air conditions of the experiment. This finding is direct contradiction of the oxygen uptake experiments where Valley Camp No. 1 was observed to be the least reactive. Thus, the conditions under which acid mine drainage is formed are quite important in establishing the reactivity of the materials.

The other coal-derived pyrites--Robena, Maple Creek, and Valley Camp No. 3--all generated sulfate as an oxidation product, although not to the degree of Valley Camp No. 1. The most acidity generated in these initial screening experiments was observed with the two commercial Kraft pyrites.

Following these initial experiments (Experiments 1 through 9 in Appendix A), the pyrites were mixed with candidate inhibitors in various configurations to determine effects in generation of pyrite oxidation products. Inhibitors considered were:

* Ground limestone,
* Iron filings,
* Iron filings - marble chips,
* Aluminum filings,
* Blast furnace slag,
* Flue gas desulfurization solids,
* Neutralized acid mine drainage solids,
* Fly ash, and
* Cement kiln dust. (The kiln dust used had a high free lime content and is different from many other kiln dusts.)

Analytical results from the sample leachates were converted into milligrams of constituent per gram of pyrite from leachate concentration/volume data. Of the several constituents analyzed for, sulfate was chosen as the key indicator of acid mine drainage formation. This choice is based on the fact that the only source of sulfate should be from pyrite oxidation, and the strong correlation between sulfate and oxygen uptake established during the oxygen uptake studies. Of the various inhibitors tested, metallic iron was the most effective in reducing sulfate generation. Inhibition effects of other agents were not noted in the relatively short times experiments were allowed to proceed.

Long-Term Experiments in Large Columns

Following these initial experiments, large columns (10-cm diameter) were filled with pyrite and with pyrite/iron nails. Approximately 5.7 kg (12.5 lb) of the Valley Camp No. 1 and Robena pyrites were placed on a 15-cm bed of sand and fibrous packing material in each of two columns. The pyrites had a depth of about 60 cm (24 in.). In addition, two companion columns containing 5.7 kg of each pyrite mixed with 1.14 kg of iron nails were fabricated to determine more precisely the inhibiting effects of metallic iron. Photographs of the 10-cm column experimental apparatus are shown in Figure 5.

Unlike the initial experiments, the studies in the 10-cm diameter columns were extended over a long period. The columns were flushed with about 1 liter of distilled water weekly and leachate analyzed for iron II, iron total, sulfate, acidity and alkalinity, and pH. Results obtained from each of the columns (converted to milligrams per kilogram) are presented in Appendix B (Valley Camp No. 1) and Appendix C (Robena).

The weekly analysis of the materials washed from the columns proved that time was needed to form large quantities of acid mine drainage in the Valley Camp No. 1 control column, but that time had little effect on acid mine drainage formation in the Robena control column. After about 8 weeks, the amount of reaction products in the Valley Camp No. 1 column had reached a plateau much higher than amounts detected in the small scale experiments or in the initial 10-cm column experiment. The iron nail-inhibited Valley Camp No. 1 column consistently produced less iron, sulfate, and acid than did the control column, whereas little difference was noted between the iron-inhibited and control columns for Robena. Thus, we obtained strong evidence that metallic iron would inhibit acid mine drainage formation from an acid-producing pyrite, but that metallic iron had virtually no effect on a pyrite which was not highly acid-productive.

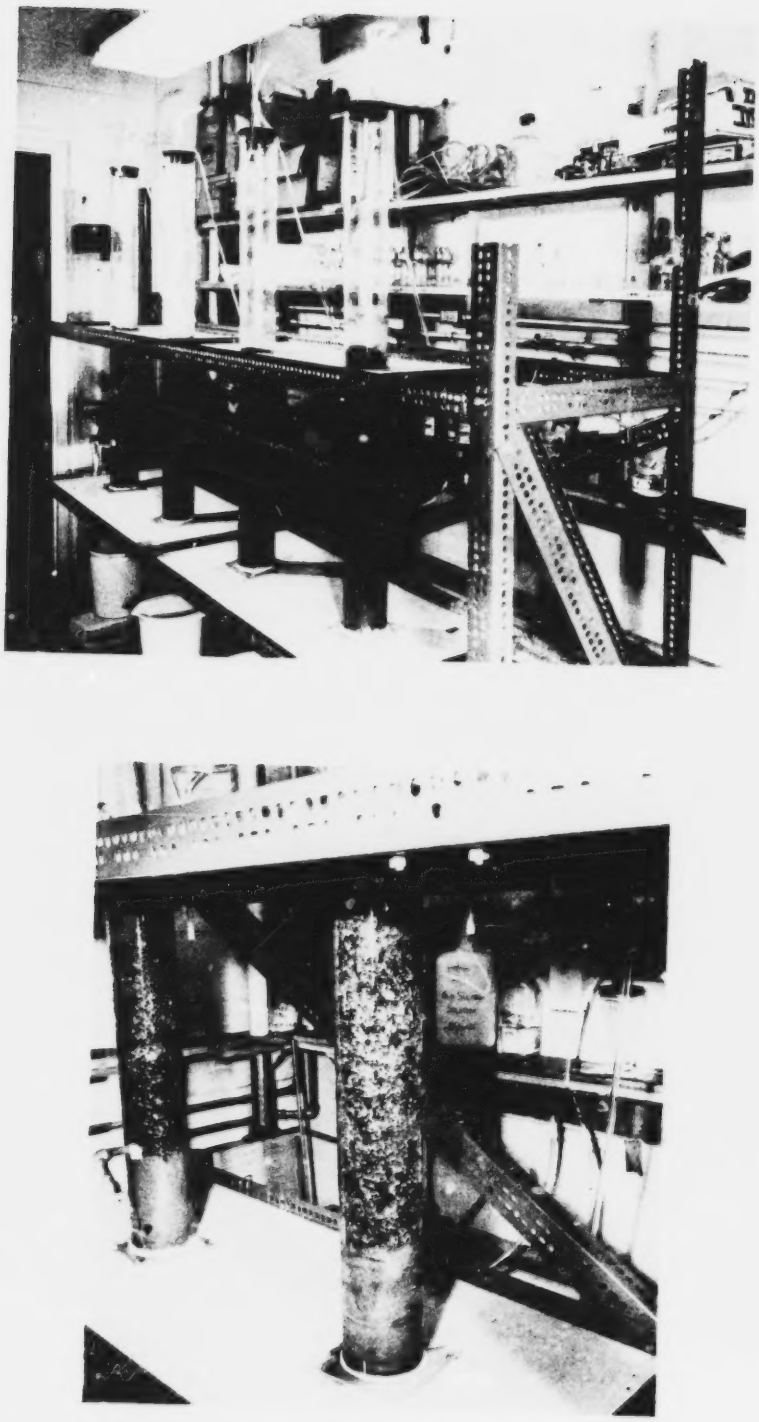


Figure 5. - 10-cm Columns used for evaluating inhibition of acid mine drainage formation.

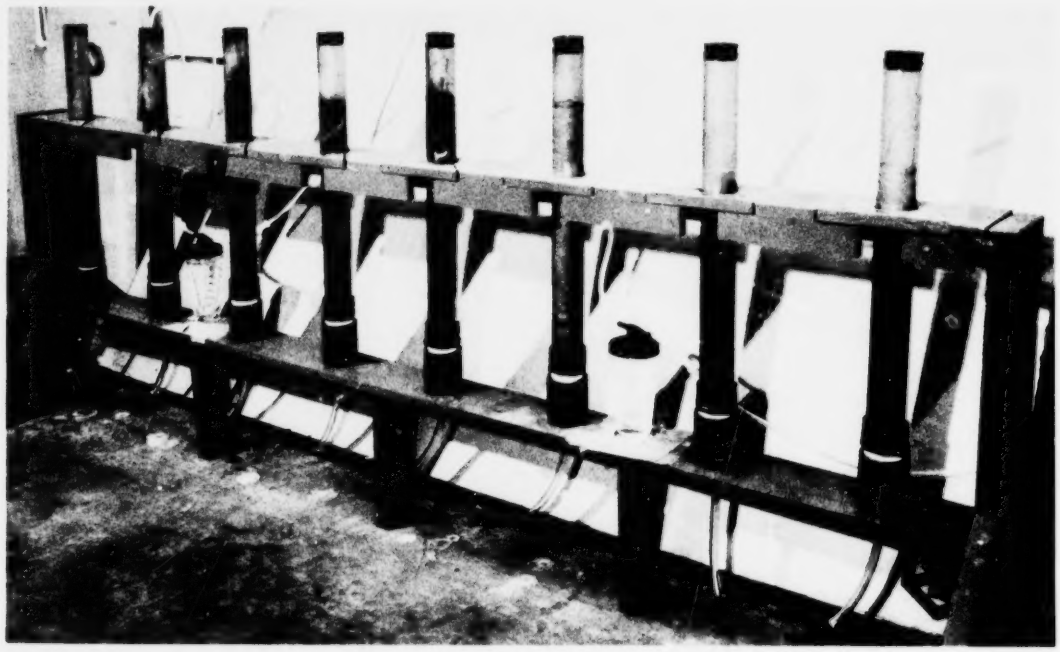
As a side experiment, leachates from the four columns were analyzed for the bacterium, Thiobacillus ferrooxidans. The leachates from the two Valley Camp columns showed bacterial colonies, and those from the two Robena columns showed none. Even when Robena columns were inoculated with thiobacillus (from the Valley Camp control columns), a culture could not be generated to promote acid production. (The effect of other bacteria was not investigated further because the program emphasis was restricted to chemical inhibition.)

With strong evidence that the Robena pyrite could not readily be made to generate acid, we proceeded to substitute Maple Creek pyrite for Robena. Furthermore, since we had evidence that time was needed for acid production to maximize, we decided that some of the inhibitors which did not appear effective in the initial experiments should be evaluated in the larger system. In order to increase the number of systems which could be evaluated simultaneously, we set up a new series of eight reaction columns of 5-cm diameter. Photographs of this apparatus are shown in Figure 6.

Four experiments with Valley Camp pyrite were undertaken in the 5-cm columns: control, iron nail-inhibited, fly ash-inhibited, and blast furnace slag-inhibited. Identical experiments in four columns containing Maple Creek pyrite were also conducted. The columns were flushed weekly with 200 ml of distilled water and analyzed for the usual components. Data from these experiments are contained in Appendix B for Valley Camp No. 1 pyrite and in Appendix C for Maple Creek pyrite.

The columns were seeded initially with leachates from the Valley Camp No. 1 10-cm column to inoculate materials with thiobacillus. There is indication that acid production in the Valley Camp No. 1 columns was affected by the inoculation but that the Maple Creek systems were not affected. Thus, it was established early that Maple Creek pyrite was not an acid producer.

After the column had become acclimated, we began to notice that the fly ash and blast furnace slag were having a pronounced effect on the amount of pyrite oxidation product--acid mine drainage products in the ash- and slag-inhibited Valley Camp pyrite were much lower than in either the control or iron nail-inhibited systems. On the other hand, ash and slag had little effect on the Maple Creek pyrite. Thus, we observed once more that inhibition can be promoted for a pyrite which is prone to generate acid mine drainage, and that inhibitors have virtually no effect on a pyrite which is not acid-producing.



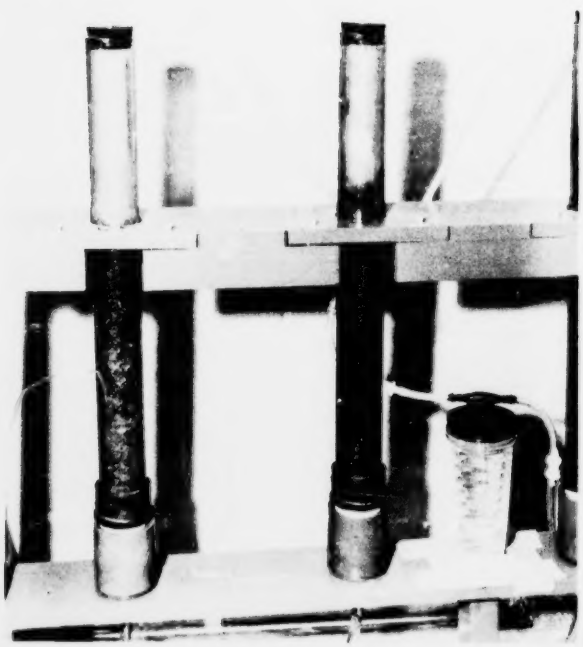


Figure 6. - 5-cm Columns used for evaluating inhibition of acid mine drainage formation.

After 14 weeks of experimentation, we decided to drop the iron nail and fly ash treated Maple Creek systems in order to free two columns for additional experimentation with Valley Camp No. 1. Since we were getting good inhibition from fly ash and blast furnace slag, we decided to test two very alkaline materials as inhibitors--portland cement and cement kiln dust (preheater fines). Results obtained for these two inhibitors for the acid-producing Valley Camp No. 1 pyrite are shown in Appendix B.

Using sulfate once again as the key indicator of acid mine drainage formation, it is clear that portland cement and kiln dust are excellent inhibitors for the Valley Camp No. 1 pyrite. The initially high sulfate levels in the kiln dust-tested system are not due to pyrite oxidation but rather from soluble sulfate in the kiln dust. We suspect that sulfate levels from the kiln dust would equilibrate to even lower sulfate concentrations if the experiments had been allowed to proceed.

As a result of the experimental work conducted during the course of the program, we conclude that the formation of acid mine drainage can be inhibited by chemical mechanisms, particularly if the innate pH of the inhibitors is high. We conclude further that pyrite which is not very susceptible to acid production will be little affected by the inhibitor.

The following section will present statistical analyses of the various sets of data generated in the experimental program so that some statistical significances of the findings are established.

INTERPRETATION OF EXPERIMENTAL DATA: VALLEY CAMP NO. 1 PYRITE

The data obtained from the 10- and 5-cm column experiments as shown in Appendix B for Valley Camp No. 1 pyrite have been analyzed statistically. The analysis consists of:

* Generation of pyritic oxidation products in control and inhibited systems as a function of time.

* Bivariate correlation of parameters in each of the systems.

* Comparison of parameter averages to determine presence of statistical difference between them.

As stated in the previous section, time is required for the various systems to reach a steady-state equilibrium with respect to generation of pyritic oxidation products. Therefore, data obtained for systems at early stages while reaching the steady-state equilibrium were not used in the statistical analyses. Such data are identified in Appendix B.

The following discussion deals with the findings of the statistical analysis of the experimental data for Valley Camp No. 1 pyrite.

The Valley Camp No. 1 pyritic systems were the most extensively evaluated because this pyrite was the one which was the most acid-producing. The first analysis undertaken was to determine rates of pyritic oxidation product generation. A bivariate regression analysis was done using the amount of product generated (in milligrams per kilogram) as the dependent variable and time (in weeks) as the independent variable.

Several curve fitting techniques were tried in order to establish which set of curves best fit the experimental data. We found that a hyperbolic function provided the best fit. The general equation for the curve is:

$$\frac{x}{y} = a + bx$$

where y = dependent variable, amount of product detected in the leachate analysis,

x = independent variable, time in weeks,

a = regression constant, and

b = regression slope.

The equations generated for the various Valley Camp No. 1 systems are shown in Table 2 along with their "r" values (correlation coefficients). All the correlation coefficients are significant at the 95% confidence level or higher with four exceptions, i.e., iron II/portland cement, iron total/fly ash, iron total/portland cement, and acidity/fly ash. The confidence levels of these four systems could be improved substantially by using another hyperbolic function of the form:

$$x \cdot y = a' + b'x$$

However, when data were plotted, there was little difference between the two hyperbolic functions, especially at long times.

The equations shown in Table 2 have been plotted in smooth curves for each of the parameters. These plots are shown in Figures 7 through 11:

* Figure 7 - Iron II versus time,

* Figure 8 - Iron total versus time,

* Figure 9 - Sulfate versus time,

* Figure 10 - Acidity versus time, and

* Figure 11 - pH versus time.

From these plots, it is apparent that fly ash, slag, portland cement, and kiln dust have a pronounced inhibiting effect on the amount of pyrite oxidation products which are generated by the Valley Camp No. 1 pyrite. The iron nail-inhibited systems show some reduction in pyrite oxidation products but not to the extent of the reduction exhibited by the more alkaline inhibitors.

The acidity plots (Figure 10) and the acidity equations (Table 2) were derived by treating alkalinity as negative acidity. Thus, the term "acidity" has been defined as the algebraic difference of acidity and alkalinity.

TABLE 2. - Regression equations relating generation of pyrite oxidation products with time: Valley Camp No. 1 pyrite

Control (N = 28)		
y = Iron II (mg/kg)	x/y = -11.216 + 0.790x	r = 0.832
y = Iron Total (mg/kg)	x/y = -0.088 + 0.008x	r = 0.919
y = Sulfate (mg/kg)	x/y = -0.018 + 0.002x	r = 0.949
y = Acidity (mg $CaCO_3$/kg)	x/y = -0.026 + 0.002x	r = 0.956
y = pH	x/y = -0.350 + 0.444x	r = 0.969
Nail Inhibited (N = 28)		
y = Iron II (mg/kg)	x/y = -16.464 + 1.076x	r = 0.704
y = Iron Total (mg/kg)	x/y = -0.146 + 0.012x	r = 0.788
y = Sulfate (mg/kg)	x/y = -0.017 + 0.002x	r = 0.855
y = Acidity (mg $CaCO_3$/kg)	x/y = -0.042 + 0.004x	r = 0.756
y = pH	x/y = -0.440 + 0.416x	r = 0.972
Fly Ash Inhibited (N = 20)		
y = Iron II (mg/kg)	x/y = 25.035 + 5.926x	r = 0.554
y = Iron Total (mg/kg)	x/y = 5.011 - 0.021x	r = -0.062
y = Sulfate (mg/kg)	x/y = -0.005 + 0.003x	r = 0.814
y = Acidity (mg $CaCO_3$/kg)	x/y = 0.192 + 0.001x	r = 0.077
y = pH	x/y = -1.039 + 0.414x	r = 0.982
Slag Inhibited (N = 20)		
y = Iron II (mg/kg)	x/y = -1265.464 + 732.292x	r = 0.505
y = Iron Total (mg/kg)	x/y = -170.404 + 28.163x	r = 0.729
y = Sulfate (mg/kg)	x/y = 0.001 + 0.003x	r = 0.937
y = Acidity (mg $CaCO_3$/kg)	x/y = -0.025 - 0.070x	r = -0.520
y = pH	x/y = 0.027 + 0.142x	r = 0.982
Portland Cement Inhibited (N = 10)		
y = Iron II (mg/kg)	x/y = -947.515 + 425.848x	r = 0.380
y = Iron Total (mg/kg)	x/y = 10.631 + 0.650x	r = 0.203
y = Sulfate (mg/kg)	x/y = -0.039 + 0.033x	r = 0.987
y = Acidity (mg $CaCO_3$/kg)	x/y = -0.006 - 0.008x	r = -0.974
y = pH	x/y = 0.003 + 0.092x	r = 0.999+

TABLE 2. - Regression equations relating generation of pyrite oxidation products with time: Valley Camp No. 1 pyrite - Continued

Kiln Dust Inhibited (N = 10)		
y = Iron II (mg/kg)	x/y = -3319.989 + 1109.686x	r = 0.738
y = Iron Total (mg/kg)	x/y = -2.914 + 6.633x	r = 0.910
y = Sulfate (mg/kg)	x/y = -0.045 + 0.014x	r = 0.956
y = Acidity (mg $CaCO_3$/kg)	x/y = 0.017 - 0.008x	r = -0.971
y = pH	x/y = -0.026 + 0.090x	r = 0.974

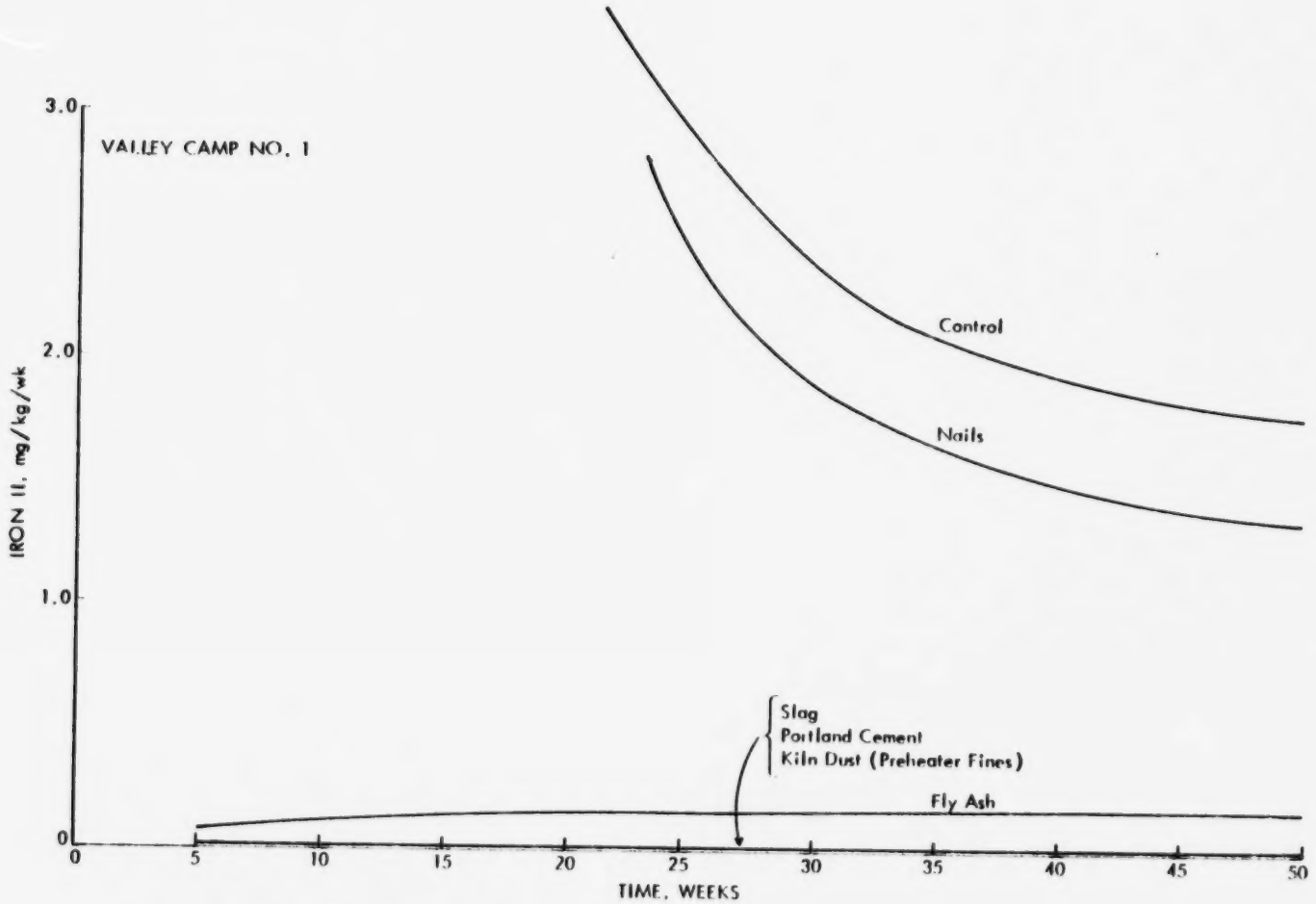


FIGURE 7. - Iron II - time plots: Valley Camp No. 1 pyrite.

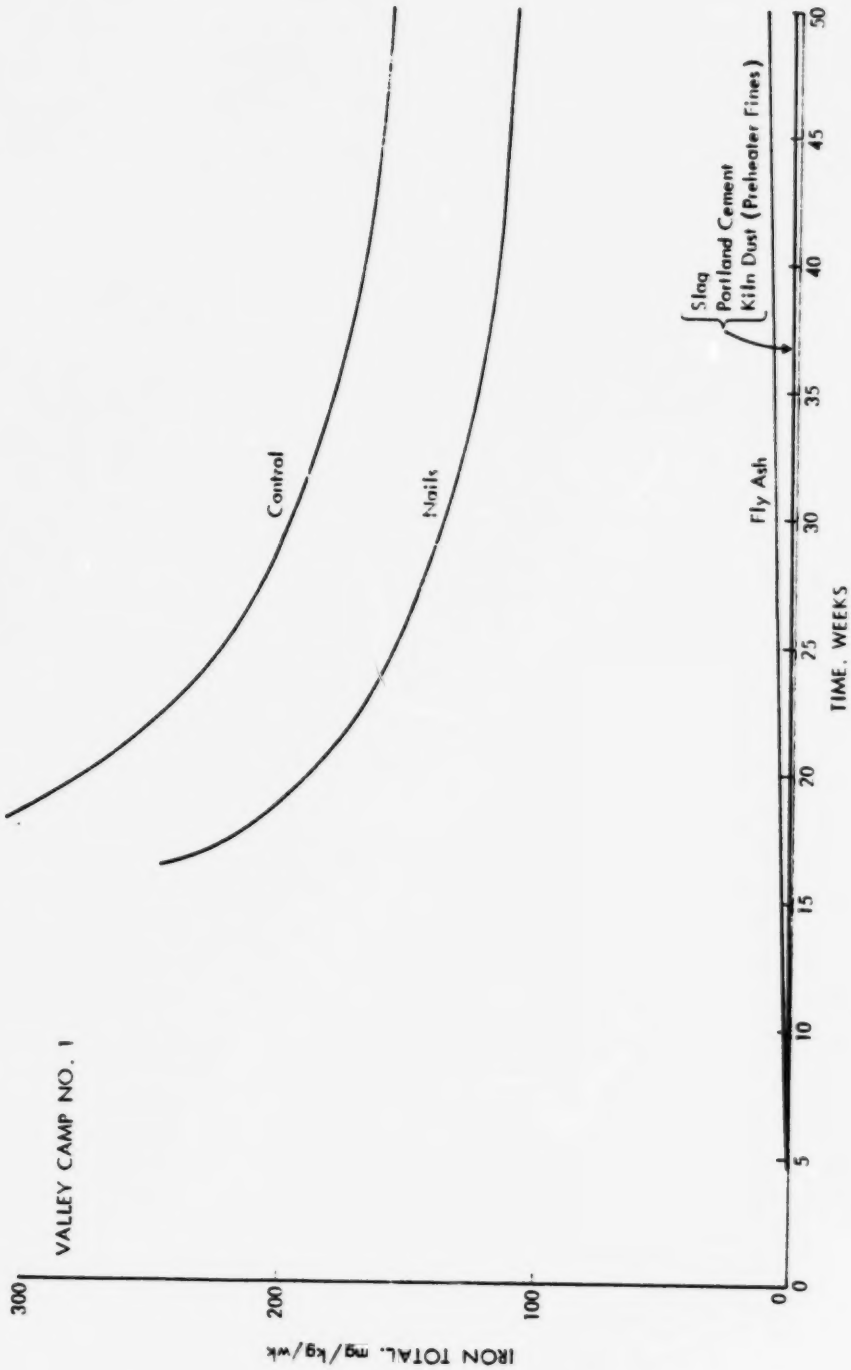


FIGURE 8. - Total iron - time plots: Valley Camp No. 1 pyrite.

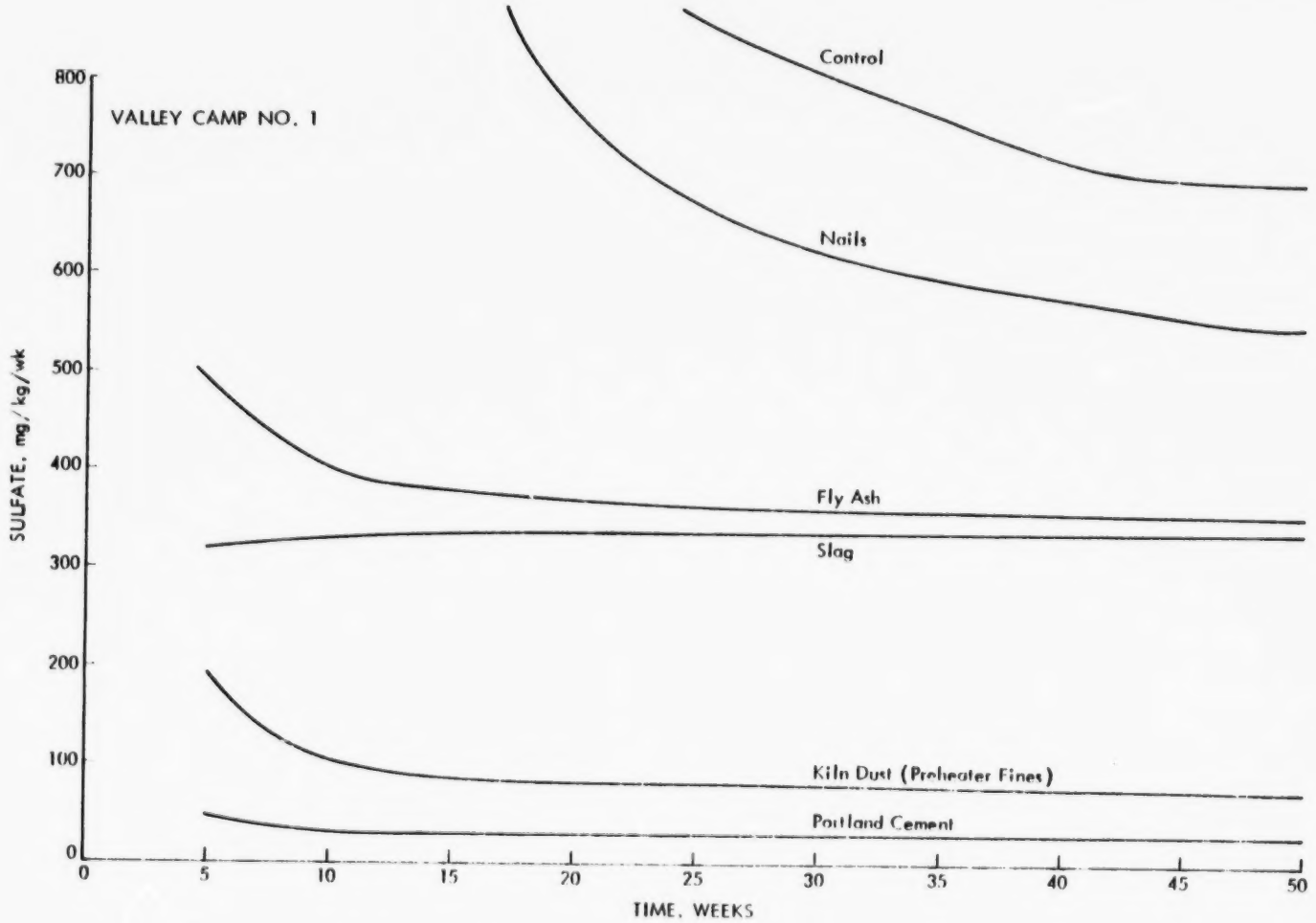


FIGURE 9. - Sulfate - time plots: Valley Camp No. 1 pyrite.

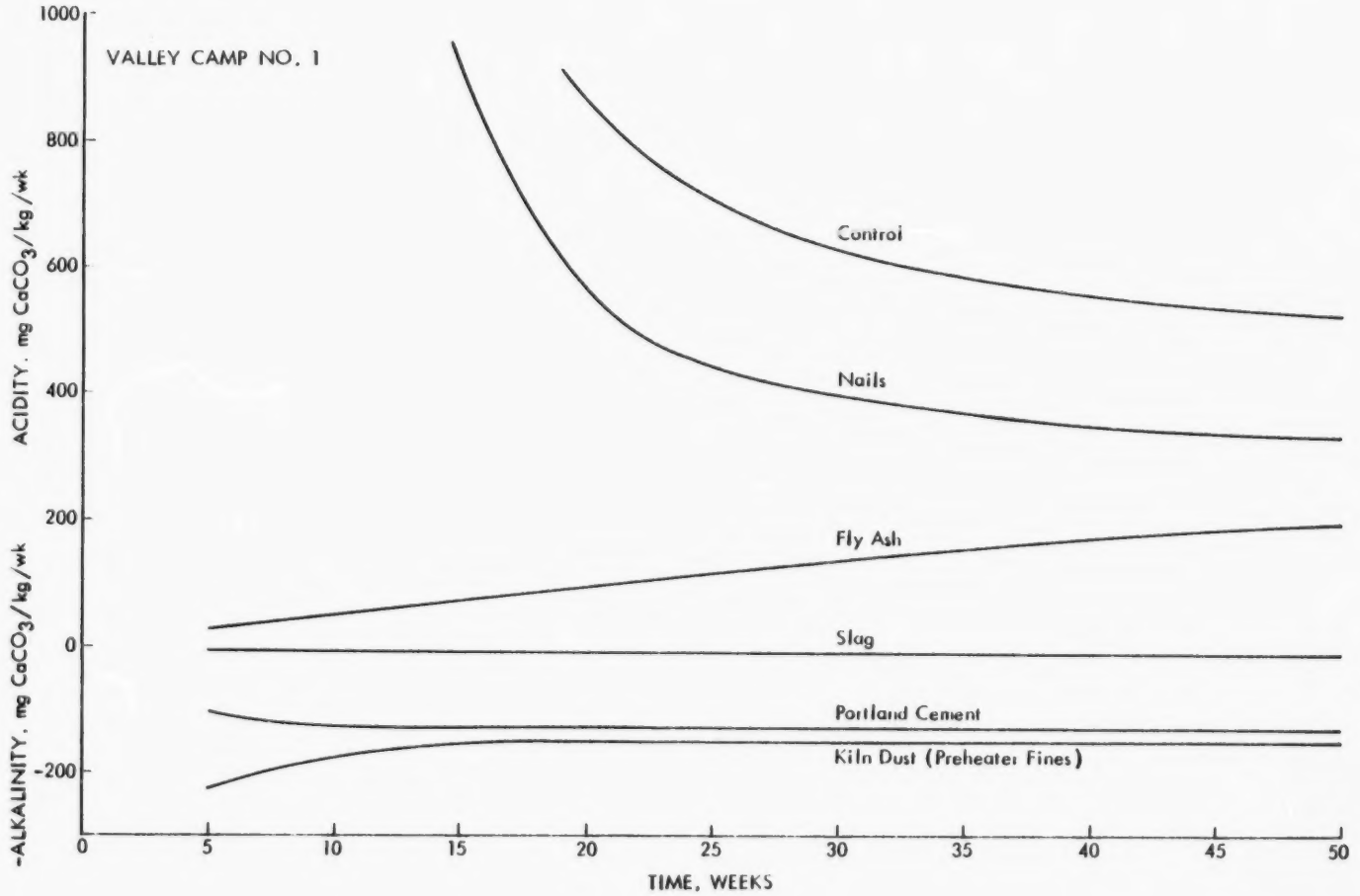


FIGURE 10. - Acidity - time plots: Valley Camp No. 1 pyrite.

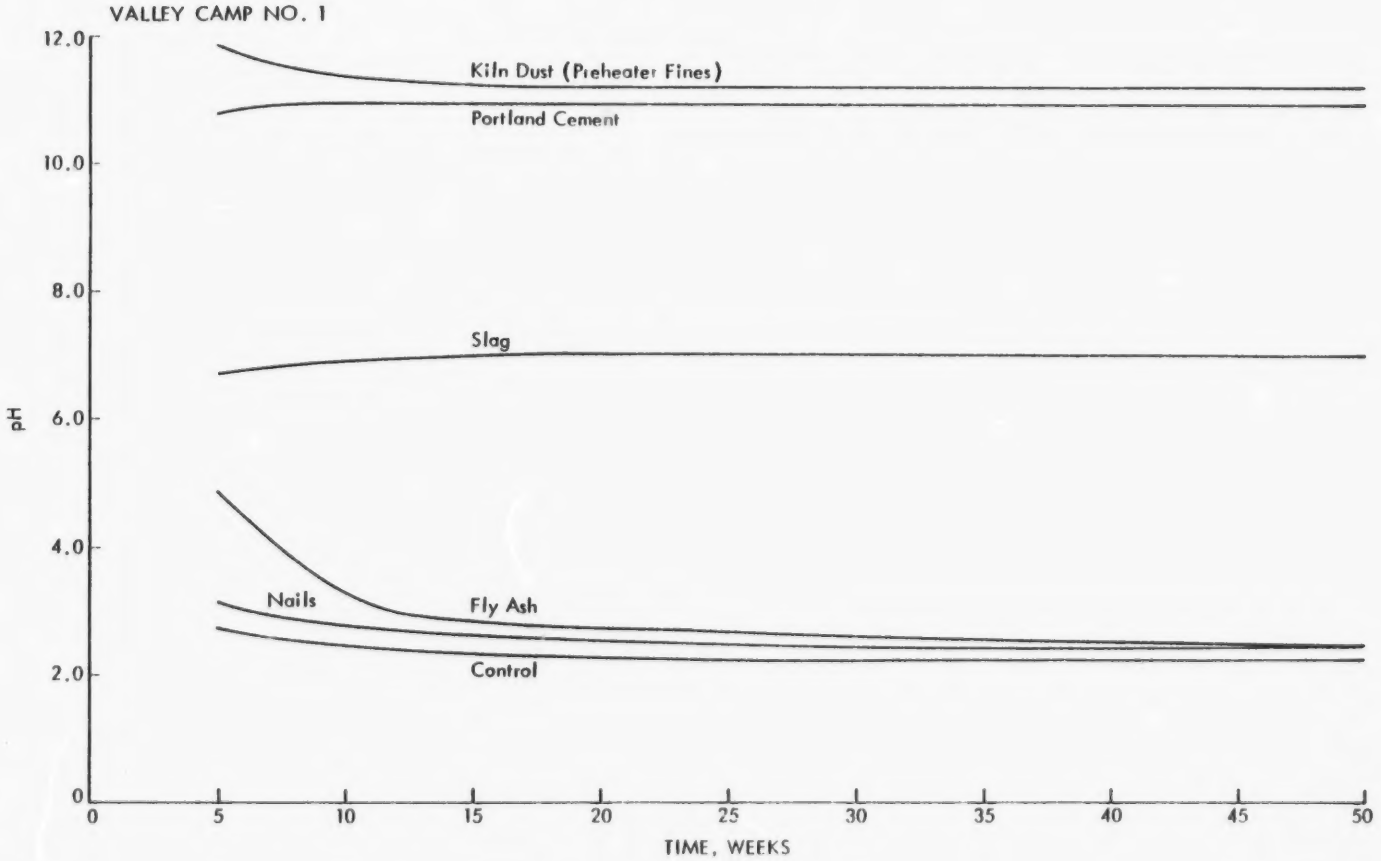
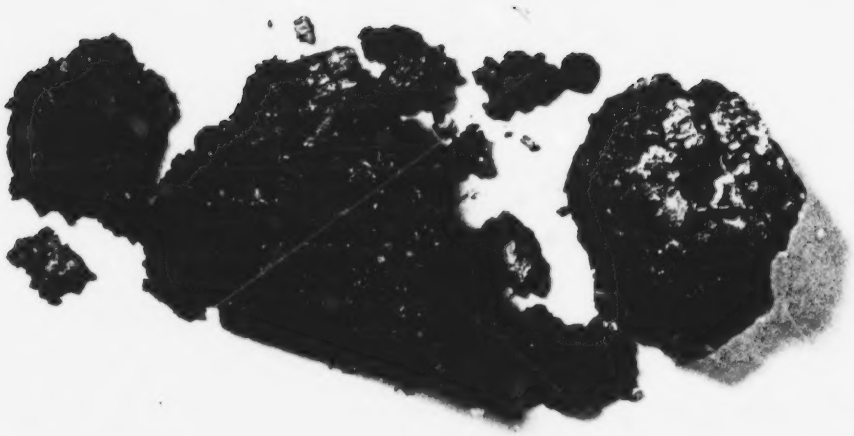


FIGURE 11. - pH - time plots: Valley Camp No. 1 pyrite.

The definition was deemed appropriate to obtain good curve fit; and because of the fact that in an alkaline system, one might be faced with overneutralization and create conditions where acid mine drainage emissions might be replaced by an equally adverse situation with excessively alkaline drainage. The acidity and pH results obtained from the portland cement and kiln dust experiments suggest that such a situation might arise in these cases. However, such a conclusion is unwarranted because of relatively short duration of the experiments (11 weeks compared to 38 weeks for the control system) which leads to a degree of uncertainty in the extrapolation to 50 weeks. We believe that alkalinity and pH would likely reach lower levels with time and that portland cement and kiln dust should not be disregarded on the basis of the limited results in this study. Certainly, the sulfate levels exhibited by portland cement are very low indicating that this material is an excellent candidate for chemical inhibition of acid mine drainage formation.

In the fly ash-inhibited system, we show that pH is not necessarily a good indicator of the amount of acid mine drainage produced. The quantities of iron, sulfate, and acidity produced in the fly ash system are comparable to the low levels produced in the slag-inhibited system; yet the pH levels are comparable to those produced in the control and iron nail-inhibited systems. These results suggest that fly ash inhibition removes buffering capacity of the system so that a small amount of pyrite oxidation product will have a pronounced effect on the pH of the water-borne emissions. It is not known at this time whether such a phenomenon is bad. When unbuffered acid mine drainage reaches a receiving stream, and if the amount of acid is small, it is very likely that the stream will be able to accommodate such emissions without much difficulty.

Upon conclusion of the experimental work, the samples of the Valley Camp No. 1 pyrite treated in various ways were photographed. These pictures are shown in Figures 12 through 14. After 38 weeks exposure to moist air and weekly leaching, the control sample (upper part of Figure 12) was encrusted with a gray, clay-like material which may bear on the decreasing levels of oxidation products noted in the experimental data. Similarly, the nail-inhibited sample (lower part of Figure 12) was coated with material which contained brownish iron oxide. The pyrite was encrusted around the nails which were badly corroded. The ash- and slag-treated samples (Figure 13) were fairly uniformly coated with inhibitor, despite the repeated leaching with distilled water. Similarly, the portland cement and kiln dust systems (Figure 14) were quite gray because of coating.



VALLEY CAMP NO. 1
CONTROL

VALLEY CAMP NO. 1
NAILS

Figure 12. - Valley Camp No. 1 pyrite: control and iron nail-inhibited after 38 weeks exposure to moist air and leaching.

VALLEY CAMP NO. 1
FLY ASH

VALLEY CAMP NO. 1
SLAG

Figure 13. - Valley Camp No. 1 pyrite: fly ash and blast furnace slag-inhibited after 25 weeks exposure to moist air and leaching.

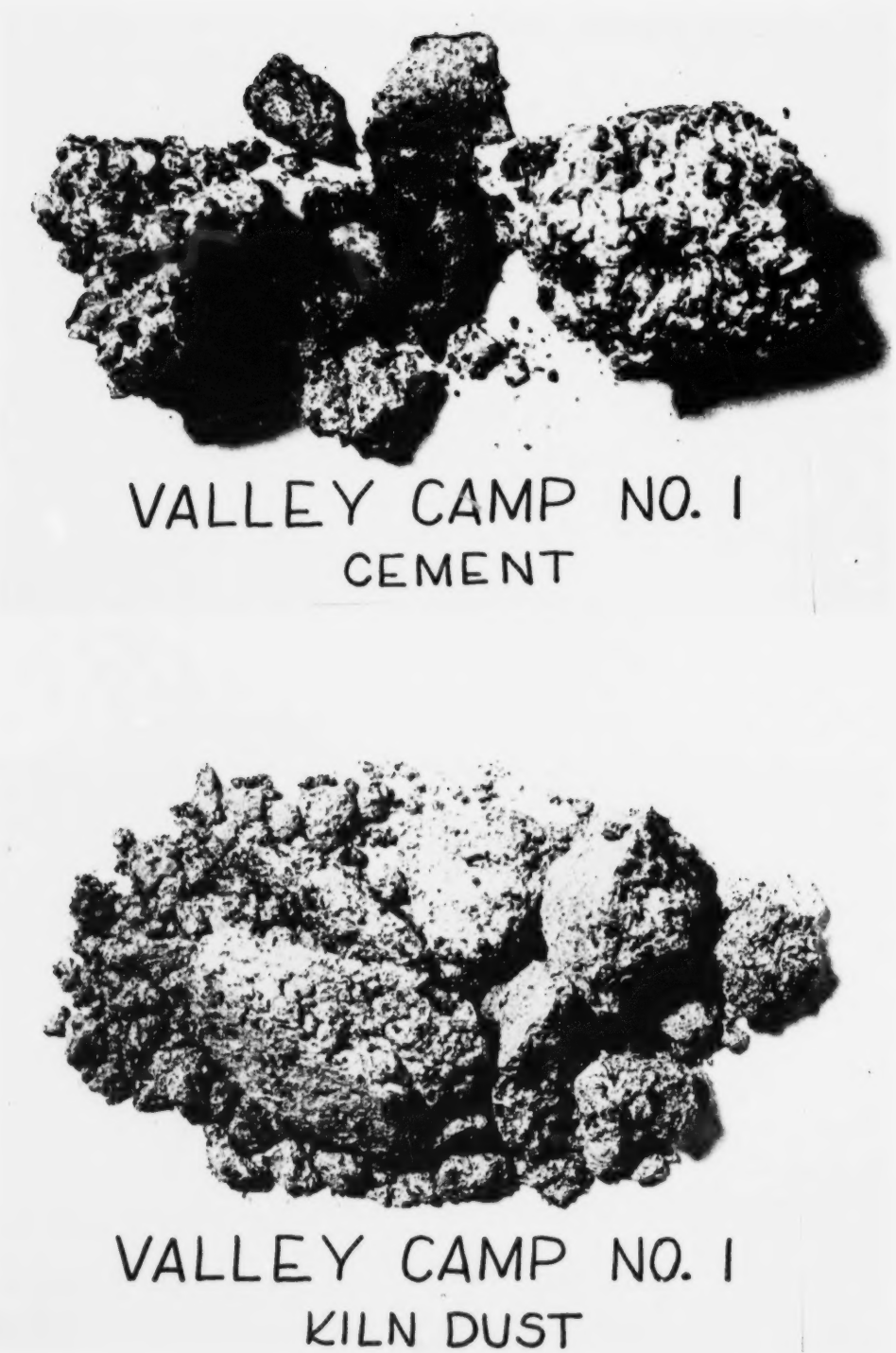


Figure 14. - Valley Camp No. 1 pyrite: portland cement and cement kiln dust-inhibited after 11 weeks exposure to moist air and leaching.

These photographs indicate that prolonged exposure to air, coupled with flushing with an equivalent of 10 cm (4 in.) of water each week does affect pyrite surfaces. The quantity of water used in the experiments might be expected to wash away the finely-divided inhibitors, yet the photographic evidence does not so indicate, nor did week-to-week observations during the study. Thus, we suggest that a dusting of exposed faces in a coal mine with an inhibiting agent such as portland cement or blast furnace slag might result in a fairly long-term control of acid mine drainage production. It appears that if an agent is truly inhibiting acid mine drainage formation, it will last for a long time. On the other hand, if the agent merely serves to neutralize or condition pyrite oxidation products, its lifetime would likely be substantially reduced.

The preceding discussion now brings us to the point where we can address the question: Are there significant relationships among the various parameters associated with acid mine drainage? From the data generated from the various systems deemed to be operating in a steady state as represented in Appendix B for Valley Camp No. 1 pyrite, we have computed averages and standard deviations for each of the constituents analyzed for in the experimental program. In addition, we have determined correlation coefficients ("r" values) between each of the parameters. These results have been tabulated in Tables 3 through 8 for each of the systems studied.

* Table 3 - Valley Camp No. 1 control,

* Table 4 - Valley Camp No. 1 iron nail-inhibited,

* Table 5 - Valley Camp No. 1 fly ash-inhibited,

* Table 6 - Valley Camp No. 1 slag-inhibited,

* Table 7 - Valley Camp No. 1 portland cement-inhibited, and

* Table 8 - Valley Camp No. 1 kiln dust inhibited.

In the control experiment (Table 3), we find that iron, sulfate, and acidity are correlated with one another but that none of these parameters correlate with pH. Thus, we have additional evidence that pH is not a good indicator of the severity of acid mine drainage problems.

TABLE 3. - Average values, standard deviations, and correlation coefficients between parameters: Valley Camp - control (N = 28)

	Iron II	Iron total	Sulfate	Acidity	pH
Iron II	AV = 27 mg/kg/wk SD = ± 42 mg/kg/wk	r = 0.620 ***	r = 0.591 **	r = 0.629 ***	r = 0.168 NS
Iron total		AV = 307 mg/kg/wk SD = ± 133 mg/kg/wk	r = 0.858 ***	r = 0.817 ***	r = 0.003 NS
Sulfate			AV = 1,147 mg/kg/wk SD = ± 395 mg/kg/wk	r = 0.973 ***	r = 0.006 NS
Acidity				AV = 986 mg/kg/wk SD = ± 437 mg/kg/wk	r = 0.089 NS
pH					AV = 2.4 SD = ± 0.2

*** Significant at 99.9% confidence level.
** Significant at 99% confidence level.
* Significant at 95% confidence level.
NS - Not significant at 95% confidence level.

TABLE 4. - Average values, standard deviations, and correlation coefficients between parameters: Valley Camp - iron nails (N = 28)

	Iron II	Iron total	Sulfate	Acidity	pH
Iron II	Av = 36 mg/kg/wk SD = ± 46 mg/kg/wk	r = 0.176 NS	r = 0.273 NS	r = 0.804 NS	r = 0.374 NS
Iron Total		Av = 234 mg/kg/wk SD = ± 110 mg/kg/wk	r = 0.599 ***	r = 0.819 ***	r = -0.086 NS
Sulfate			Av = 797 mg/kg/wk SD = ± 227 mg/kg/wk	r = 0.864 ***	r = -0.094 NS
Acidity				Av = 655 mg/kg/wk SD = ± 262 mg/kg/wk	r = -0.154 NS
pH					Av = 2.6 SD = ± 0.3

*** Significant at 99.9% confidence level.
** Significant at 99% confidence level.
* Significant at 95% confidence level.
NS - Not significant at 95% confidence level.

TABLE 5. - Average values, standard deviations, and correlation coefficients between parameters: Valley Camp - fly ash (N = 20)

	Iron II	Iron total	Sulfate	Acidity	pH
Iron II	Av = 0.16 mg/kg/wk SD = ± 0.08 mg/kg/wk	r = 0.445 *	r = -0.269 NS	r = 0.253 NS	r = 0.306 NS
Iron Total		Av = 4.1 mg/kg/wk SD = ± 2.2 mg/kg/wk	r = -0.085 NS	r = 0.456 *	r = -0.516 *
Sulfate			Av = 425 mg/kg/wk SD = ± 123 mg/kg/wk	r = -0.044 NS	r = 0.642 **
Acidity				Av = 88 mg/kg/wk SD = ± 45 mg/kg/wk	r = -0.583 **
pH					Av = 4.2 SD = ± 0.8

** Significant at 99% confidence level.
* Significant at 95% confidence level.
NS - Not significant at 95% confidence level.

TABLE 6. - Average values, standard deviations, and correlation coefficients between parameters: Valley Camp - slag (N = 20)

	Iron II	Iron total	Sulfate	Acidity[a/]	pH
Iron II	Av = 0.008 mg/kg/wk SD = ± 0.020 mg/kg/wk	r = 0.008 NS	r = -0.248 NS	r = -0.183 NS	r = 0.077 NS
Iron Total		Av = 0.20 mg/kg/wk SD = ± 0.40 mg/kg/wk	r = -0.052 NS	r = -0.105 NS	r = 0.187 NS
Sulfate			Av = 348 mg/kg/wk SD = ± 81 mg/kg/wk	r = 0.188 NS	r = -0.017 NS
Acidity[a/]				Av = -16 mg/kg/wk SD = ± 5 mg/kg/wk	r = -0.412 NS
pH					Av = 7.0 SD = ± 0.4

a/ Alkalinity = - acidity.
NS - Not significant at 95% confidence level.

TABLE 7. - Average values, standard deviations, and correlation coefficients between parameters: Valley Camp - portland cement (N = 10)

	Iron II	Iron Total	Sulfate	Acidity[a/]	pH
Iron II	Av = 0.03 mg/kg/wk SD = ± 0.03 mg/kg/wk	r = 0.292 NS	r = 0.276 NS	r = 0.288 NS	r = 0.569 NS
Iron Total		Av = 0.62 mg/kg/wk SD = ± 0.46 mg/kg/wk	r = 0.350 NS	r = 0.220 NS	r = 0.154 NS
Sulfate			Av = 44 mg/kg/wk SD = ± 18 mg/kg/wk	r = 0.-689 *	r = -0.769 **
Acidity[a/]				Av = -115 mg/kg/wk SD = ± 20 mg/kg/wk	r = 0.766 **
pH					Av = 10.8 SD = ± 0.2

a/ Alkalinity = - acidity.
** Significant at 99% confidence level.
* Significant at 95% confidence level.
NS = Not significant at 95% confidence level.

TABLE 8. - Average values, standard deviations, and correlation coefficients between parameters: Valley Camp - kiln dust (preheater fires) (N = 10)

	Iron II	Iron total	Sulfate	Acidity[a/]	pH
Iron II	Av = 0.03 mg/kg/wk SD = ± 0.04 mg/kg/wk	r = 0.215 NS	r = 0.359 NS	r = 0.768 AA	r = 0.305 NS
Iron Total		Av = 0.28 mg/kg/wk SD = ± 0.39 mg/kg/wk	r = 0.132 NS	r = 0.476 NS	r = 0.645 A
Sulfate			Av = 328 mg/kg/wk SD = ± 272 mg/kg/wk	r = 0.738 A	r = 0.853 AA
Acidity[a/]				Av = -237 mg/kg/wk SD = ± 69 mg/kg/wk	r = 0.798 AA
pH					Av = 11.8 SD = ± 0.4

a/ Alkalinity = - acidity.
** Significant at 99% confidence level.
* Significant at 95% confidence level.
NS = Not significant at 95% confidence level.

In the nail-inhibited system (Table 4), we find that total iron, sulfate, and acidity correlate with each other but that none of these constituents correlate with ferrous iron or pH. This observation suggests that total iron is an important indicator of the amount of acid mine drainage produced.

The fly ash-inhibited system (Table 5) indicates weak correlation (95%) between iron II and total iron, acidity and total iron, and pH and total iron. Somewhat stronger correlations (99%) are noted between pH and sulfate, and pH and acidity. No significant correlations are noted between the remaining parameter pairs.

The slag-inhibited system (Table 6) shows no significant correlations between parameter pairs, suggesting that acid mine drainage formation has been effectively inhibited in this system.

Finally, portland cement (Table 7) and kiln dust (Table 8) show correlations among sulfate, alkalinity, and pH. (The kiln dust system shows correlations in the acidity/iron II and pH/iron total couples; however, the correlations are not believed to be important because of the low levels of iron.) The sulfate, alkalinity, and pH relationships are believed to arise from the alkaline conditions of these two inhibitors.

The averages of each parameter for each system have been plotted on a linear scale to show relative effects of the inhibitors. This plot is presented in Figure 15. From this plot, we can readily see that marked differences in averages appear among the parameters for the inhibited systems compared to the control. However, the standard deviations shown in Tables 3 through 8 are wide, indicating that despite absolute values of averages, there might not be any real differences. Thus, the means have been compared using methods described by Brownlee (2). This method calculated the "Student t" value for a pair of averages. If the "t" value exceeds that of the value established for the appropriate number of degrees of freedom in the "Student t" table, then difference between the averages of the two paired components is significant.

The basic arithmetic is as follows:

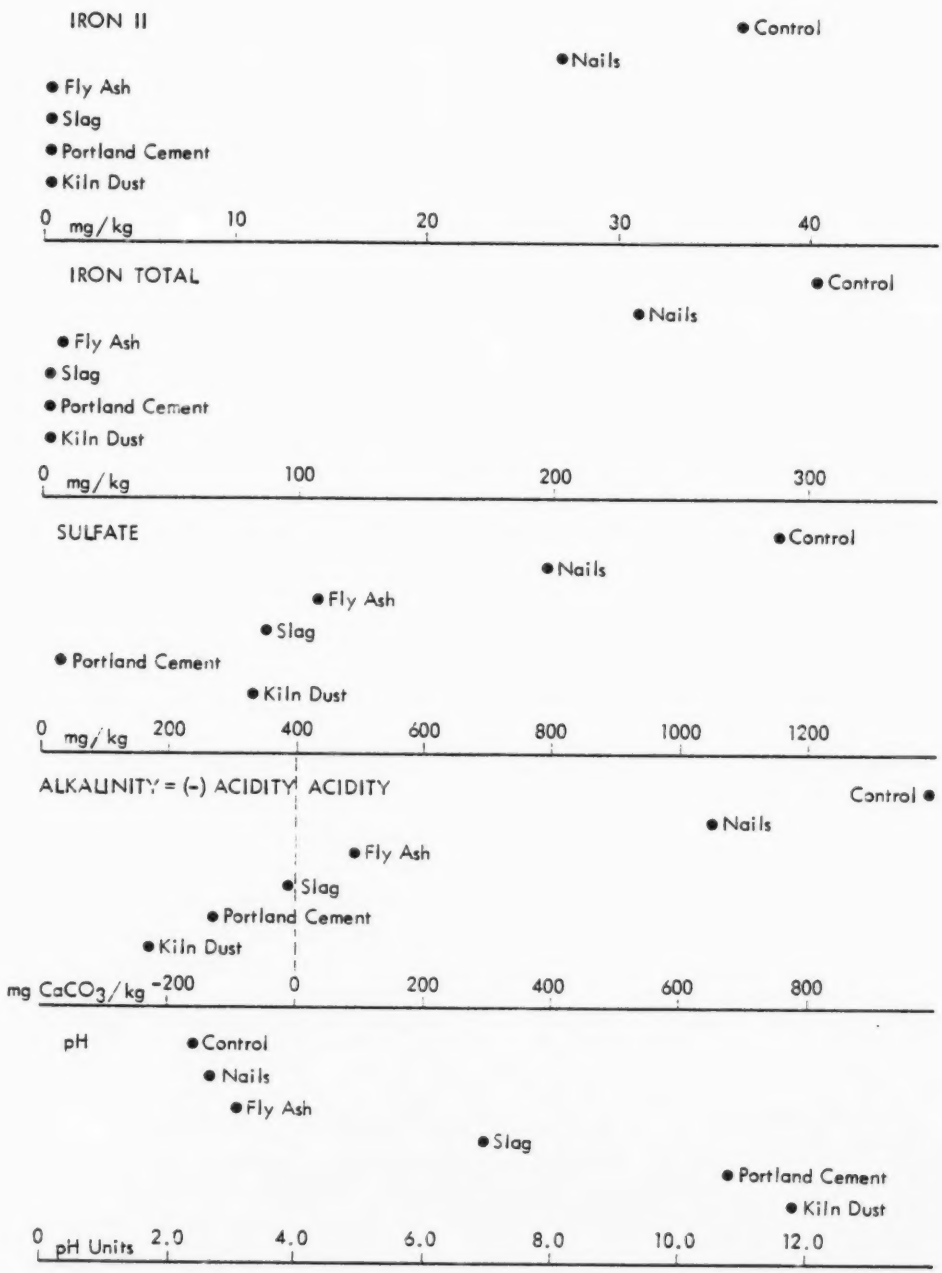


FIGURE 15. - Summary of average values: Valley Camp No. 1 pyrite.

$$\bar{x}_i = \frac{\Sigma x_i}{n_1} \; ; \; \bar{x}_j = \frac{\Sigma x_j}{n_2}$$

$$\sigma^2 = \left[\Sigma x_i^2 - \frac{(\Sigma x_i)^2}{n_1} + \Sigma x_j^2 - \frac{(\Sigma x_j)^2}{n_2} \right] (n_1 + n_2 - 2)$$

$$t = \left| \frac{\bar{x}_i - \bar{x}_j}{\sigma} \sqrt{\frac{n_1 \times n_2}{n_1 + n_2}} \right|$$

where Σx_i = sum of constituent i,

Σx_j = sum of constituent j,

Σx_i^2 = sum of squares of constituent i,

Σx_j^2 = sum of squares of constituent j,

n_1 = number of data for constituent i, and

n_2 = number of data for constituent j.

The results of this comparison for the Valley Camp No. 1 pyrite systems are presented in Table 9. This table compares averages for each constituent for the 15 pairs arising from control and five inhibitor experiments. As can be seen from the table, all of the averages from the inhibited systems are statistically different at a confidence level greater than 99.9% in most cases from the averages of the control. Thus, we conclude that acid mine drainage formation in the Valley Camp No. 1 pyrite has been effectively inhibited by the chemicals evaluated.

Similarly, the averages observed for the nail-inhibited experiments are significantly different from the averages obtained from those obtained from the other inhibitors. Thus, we conclude that fly ash, slag, portland cement, and kiln dust are more effective inhibitors than is metallic iron.

Fly ash inhibition is seen to be statistically different from slag, portland cement, and kiln dust. On the other hand, iron averages of the pairs associated with slag, portland cement, and kiln dust are shown not to be different. The nonsignificance of sulfate averages for the fly ash/kiln dust and slag/kiln dust couples is likely due in part to the high levels of sulfate originally present in the kiln dust.

TABLE 9. - Statistical comparison of averages by inhibitor: Valley Camp pyrite

System:	Control/Iron Nails ($n_c + n_n - 2 = 54$)				
Iron II:	Av_c = 27;	Av_n = 36;	t = 0.78;	NS
Iron Total:	Av_c = 307;	Av_n = 234;	t = 2.25;	*
Sulfate:	Av_c = 1,147;	Av_n = 797;	t = 4.08;	***
Acidity:	Av_c = 986;	Av_n = 644;	t = 3.55;	***
pH:	Av_c = 2.4;	Av_n = 2.6;	t = 3.10;	**
System:	Control/Fly Ash ($n_c + n_f - 2 = 46$)				
Iron II:	Av_c = 27;	Av_f = 0.16;	t = 2.89;	**
Iron Total:	Av_c = 307;	Av_f = 4.1;	t = 10.14;	***
Sulfate:	Av_c = 1,147;	Av_f = 425;	t = 7.90;	***
Acidity:	Av_c = 986;	Av_f = 88;	t = 10.90;	***
pH:	Av_c = 2.4;	Av_f = 3.2;	t = 4.79;	***
System:	Control/Slag ($n_c + n_s - 2 = 46$)				
Iron II:	Av_c = 27;	Av_s = 0.008;	t = 2.91;	**
Iron Total:	Av_c = 307;	Av_s = 0.20;	t = 10.68;	***
Sulfate:	Av_c = 1,147;	Av_s = 348;	t = 9.56;	***
Acidity:	Av_c = 986;	Av_s = - 16;	t = 10.97;	***
pH:	Av = 2.4;	Av = 7.0;	t = 48.13;	***
System:	Control/Portland Cement ($n_c + n_p - 2 = 36$)				
Iron II:	Av_c = 27;	Av_p = 0.03;	t = 5.54;	***
Iron Total:	Av_c = 307;	Av_p = 0.62;	t = 19.57;	***
Sulfate:	Av_c = 1,147;	Av_p = 44;	t = 23.79;	***
Acidity:	Av_c = 986;	Av_p = - 115;	t = 21.41;	***
pH:	Av_c = 2.4;	Av_p = 10.8;	t = 291.81;	***
System:	Control/Kiln Dust ($n_c + n_d - 2 = 36$)				
Iron II:	Av_c = 27;	Av_d = 0.03;	t = 5.54;	***
Iron Total:	Av_c = 307;	Av_d = 0.28;	t = 19.59;	***
Sulfate:	Av_c = 1,147;	Av_d = 328;	t = 16.41;	***

TABLE 9. - Statistical comparison of averages by inhibitor: Valley Camp pyrite - Continued

Acidity:	Av_c = 986;	Av_d = - 237;	t = 23.70;	***
pH:	Av_c = 2.4;	Av_d = 11.8;	t = 256.79;	***
System:	Iron Nails/Fly Ash ($n_n + n_f - 2 = 46$)			
Iron II:	Av_n = 36;	Av_f = 0.16;	t = 3.50;	**
Iron Total:	Av_n = 234;	Av_f = 4.1;	t = 9.30;	***
Sulfate:	Av_n = 797;	Av_f = 425;	t = 6.66;	***
Acidity:	Av_n = 644;	Av_f = 88;	t = 9.38;	***
pH:	Av_n = 2.6;	Av_f = 3.2;	t = 3.53;	***
System:	Iron Nails/Slag ($n_n + n_s = 2 = 46$)			
Iron II:	Av_n = 36;	Av_s = 0.008;	t = 3.51;	**
Iron Total:	Av_n = 234;	Av_s = 0.20;	t = 9.46;	***
Sulfate:	Av_n = 797;	Av_s = 348;	t = 8.47;	***
Acidity:	Av_n = 644;	Av_s = - 16;	t = 11.25;	***
pH:	Av_n = 2.6;	Av_s = 7.0;	t = 43.87;	***
System:	Iron Nails/Portland Cement ($n_n + n_p - 2 = 36$)			
Iron II:	Av_n = 36;	Av_p = 0.03;	t = 2.45;	*
Iron Total:	Av_n = 234;	Av_p = 0.62;	t = 6.64;	***
Sulfate:	Av_n = 797;	Av_p = 44;	t = 10.41;	***
Acidity:	Av_n = 644;	Av_p = - 115;	t = 9.08;	***
pH:	Av_n = 2.6;	Av_p = 10.8;	t = 91.96;	***
System:	Iron Nails/Kiln Dust ($n_n + n_p - 2 = 36$)			
Iron II:	Av_n = 36;	Av_p = 0.03;	t = 2.47;	*
Iron Total:	Av_n = 234;	Av_p = 0.28;	t = 6.65;	***
Sulfate:	Av_n = 797;	Av_p = 328;	t = 5.33;	***
Acidity:	Av_n = 644;	Av_p = - 237;	t = 10.43;	***
pH:	Av_n = 2.6;	Av_p = 11.8;	t = 84.93;	***
System:	Fly Ash/Slag ($n_f + n_s - 2 = 38$)			
Iron II:	Av_f = 0.16;	Av_s = 0.008;	t = 8.12;	***
Iron Total:	Av_f = 4.1;	Av_s = 0.20;	t = 7.71;	***

TABLE 9. - Statistical comparison of averages by inhibitor: Valley Camp pyrite - Continued

Sulfate:	Av_f =	425;	Av_s =	348;	t =	2.34;	*
Acidity:	Av_f =	88;	Av_s =	- 16;	t =	10.17;	***
pH:	Av_f =	3.2;	Av_s =	7.0;	t =	18.00;	***
System:	Fly Ash/Portland Cement ($n_f + n_p - 2 = 28$)						
Iron II:	Av_f =	0.16;	Av_p =	0.03;	t =	5.03;	***
Iron Total:	Av_f =	4.1;	Av_p =	0.62;	t =	4.85;	***
Sulfate:	Av_f =	425;	Av_p =	44;	t =	9.64;	***
Acidity:	Av_f =	88;	Av_p =	- 115;	t =	13.35;	***
pH:	Av_f =	3.2;	Av_p =	10.8;	t =	28.23;	***
System:	Fly Ash/Kiln Dust ($n_f + n_d - 2 = 28$)						
Iron II:	Av_f =	0.16;	Av_d =	0.03;	t =	4.94;	***
Iron Total:	Av_f =	4.1;	Av_d =	0.28;	t =	5.35;	***
Sulfate:	Av_f =	425;	Av_d =	328;	t =	1.35;	NS
Acidity:	Av_f =	88;	Av_d =	- 237;	t =	15.48;	***
pH:	Av_f =	3.2;	Av_d =	11.8;	t =	30.71;	***
System:	Slag/Portland Cement ($n_s + n_p - 2 = 28$)						
Iron II:	Av_s =	0.008;	Av_p =	0.03;	t =	2.02;	NS
Iron Total:	Av_s =	0.20;	Av_p =	0.62;	t =	2.54;	*
Sulfate:	Av_s =	348;	Av_p =	44;	t =	33.61;	***
Acidity:	Av_s =	- 16;	Av_p =	- 115;	t =	20.89;	***
pH:	Av_s =	7.0;	Av_p =	10.8;	t =	26.67;	***
System:	Slag/Kiln Dust ($n_s + n_d - 2 = 28$)						
Iron II:	Av_s =	0.008;	Av_d =	0.03;	t =	1.75;	NS
Iron Total:	Av_s =	0.20;	Av_d =	0.28;	t =	0.48;	NS
Sulfate:	Av_s =	348;	Av_d =	328;	t =	0.30;	NS
Acidity:	Av_s =	- 16;	Av_d =	- 237;	t =	14.49;	***
pH:	Av_s =	7.0;	Av_d =	11.8;	t =	29.80;	***

TABLE 9. - Statistical comparison of averages by inhibotor: Valley Camp pyrite - Continued

System: Portland Cement/Kiln Dust ($n_p + n_d - 2 = 18$)							
Iron II:	Av_p =	0.03;	Av_d =	0.03;	t =	0.00;	NS
Iron Total:	Av_p =	0.62;	Av_d =	0.28;	t =	1.78;	NS
Sulfate:	Av_p =	44;	Av_d =	328;	t =	3.30;	**
Acidity:	Av_p =	- 115;	Av_d =	- 237;	t =	5.38;	***
pH:	Av_p =	10.8;	Av_d =	11.8;	t =	7.22;	***

Subscript c = Control
Subscript n = Iron nails
Subscript f = Fly ash
Subscript s = Slag
Subscript p = Portland cement
Subscript d = Kiln dust
t = "Student" t
*** Significant at 99.9% confidence level.
** Significant at 99% confidence level.
* Significant at 95% confidence level.
NS Not significant at 95% confidence level.

In a later section of this report (p. 90), the experimental data have been analyzed in terms of chemical stoichiometry, i.e., the number of moles of pyrite oxidized to generate the quantities of reaction products determined during the weekly analyses. This analysis clearly shows that less pyrite is oxidized in the Valley Camp No. 1 inhibited systems than was oxidized in the control columns. The smaller quantity of pyrite oxidized has been interpreted as chemical inhibition of acid mine drainage formation.

INTERPRETATION OF EXPERIMENTAL DATA: LOW-ACID-PRODUCING PYRITES

As described in the earlier experimental procedures section, experimental results obtained from the Robena and Maple Creek pyrites were inconclusive because of the inability to get much acid generation in the untreated pyrites. This observation is confirmed when data are analyzed in the manner just described for Valley Camp No. 1 pyrite.

Robena Pyrite

The steady-state data for the two experiments (control and nail-inhibited) using Robena pyrite and presented in Appendix C were subjected to bivariate regression analysis to develop oxidation product-time curves fitting a hyperbolic equation of the type:

$$\frac{x}{y} = a + bx$$

The equations generated are presented in Table 10.

These equations were then plotted as a function of time for each parameter. The plots were shown in Figures 16 through 20.

* Figure 16 - Iron II versus time: Robena pyrite,
* Figure 17 - Iron total versus time: Robena pyrite,
* Figure 18 - Sulfate versus time: Robena pyrite,
* Figure 19 - Acidity versus time: Robena pyrite, and
* Figure 20 - pH versus time: Robena pyrite.

These plots show little difference between the control sample and the nail-inhibited sample. The y-axis of the Robena plots have been greatly expanded from those for the Valley Camp No. 1 (Figures 7 through 11). Thus, differences between the control and nail-inhibited experiments are quite small compared to those of the more acid-producing pyrite. As will be shown later, a real difference may be present in the iron II case.

TABLE 10. - Regression equations relating generation of pyrite oxidation products with time: Robena pyrite

Control (N = 13):		
y = Iron II (mg/kg)	x/y = 2468.718 + 34.066x	r = 0.041
y = Iron Total (mg/kg)	x/y = 10.892 + 7.831x	r = 0.473
y = Sulfate (mg/kg)	x/y = 0.001 + 0.003x	r = 0.980
y = Acidity (mg $CaCO_3$/kg)	x/y = -0.419 + 0.032x	r = 0.138
y = pH	x/y = -0.056 + 0.160x	r = 0.992
Nail Inhibited (N = 13)		
y = Iron II (mg/kg)	x/y = 1338.462 + 681.319x	r = 0.666
y = Iron Total (mg/kg)	x/y = 29.764 + 54.588x	r = 0.605
y = Sulfate (mg/kg)	x/y = 0.003 + 0.003x	r = 0.960
y = Acidity (mg $CaCO_3$/kg)	x/y = -0.278 + 0.113x	r = 0.377
y = pH	x/y = -0.021 + 0.154x	r = 0.987

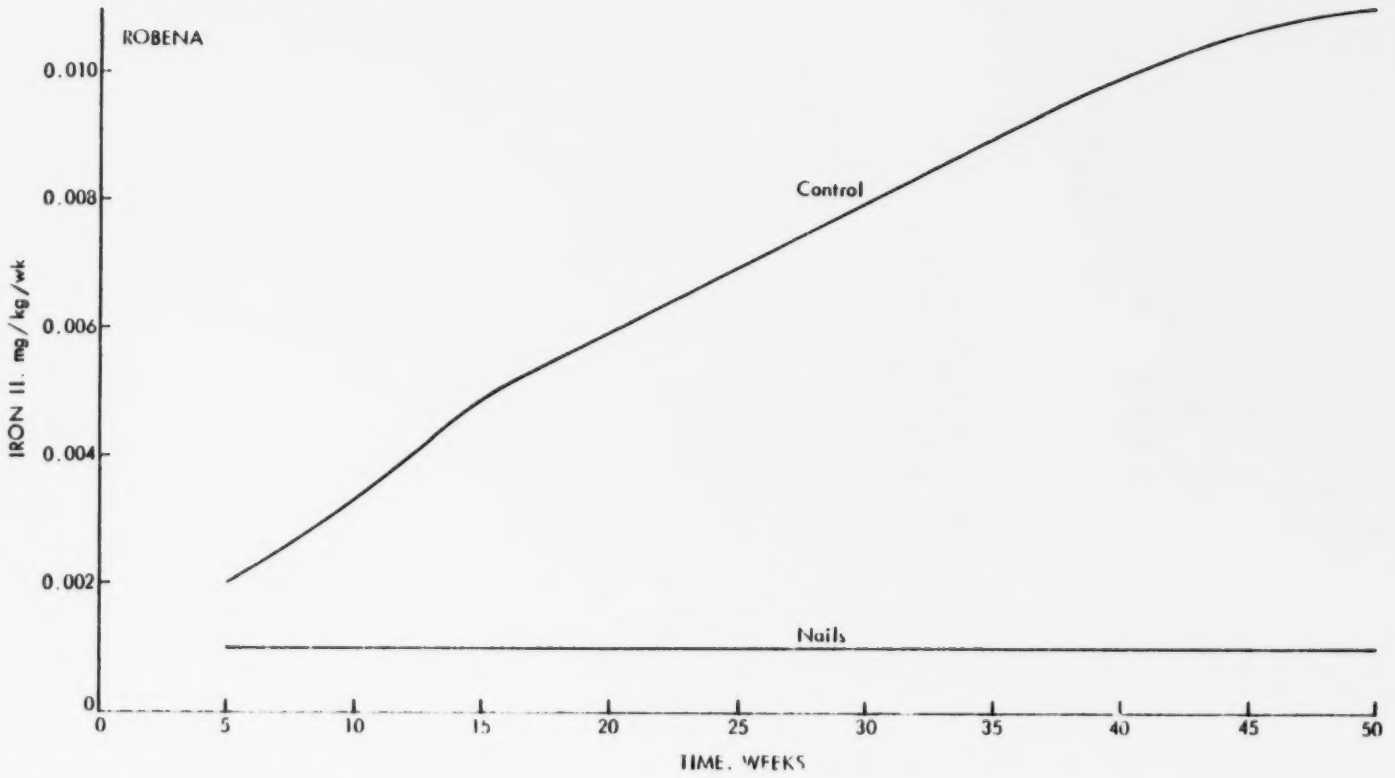


FIGURE 16. - Iron II - time plots: Robena pyrite.

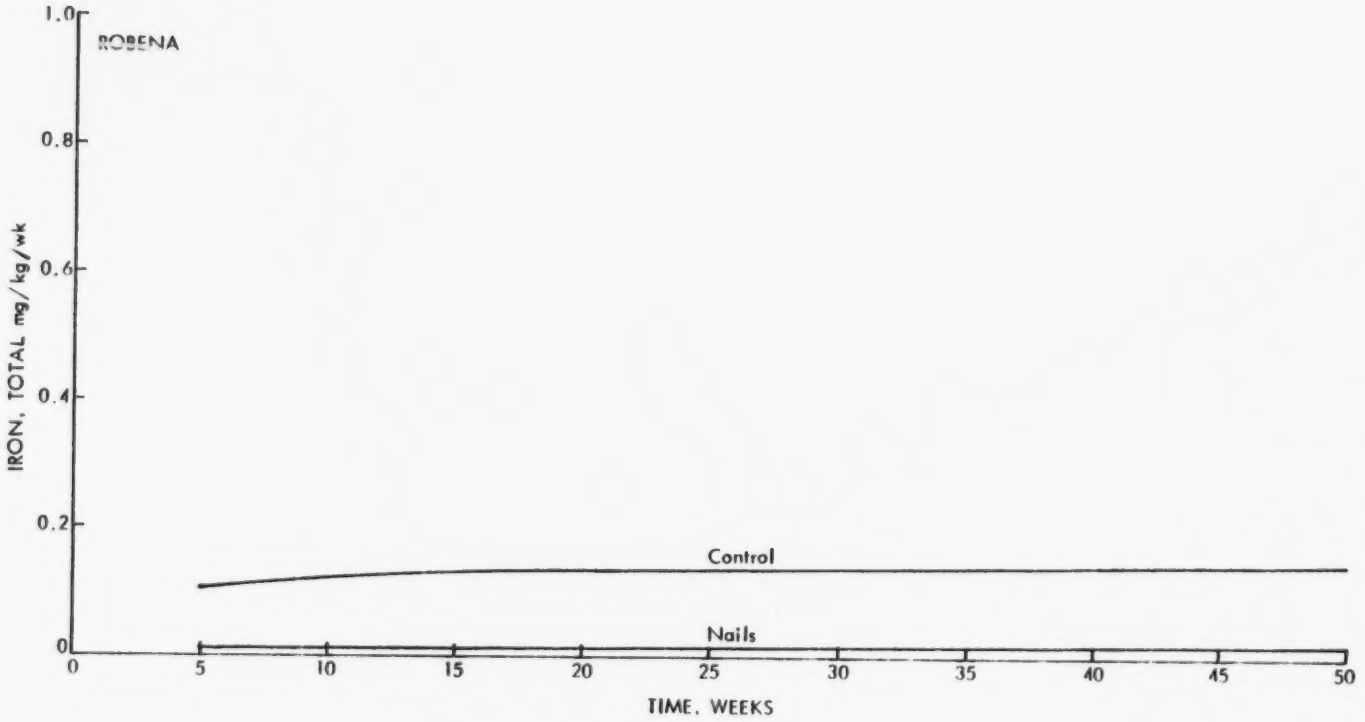


FIGURE 17. - Iron total versus time plots: Robena pyrite.

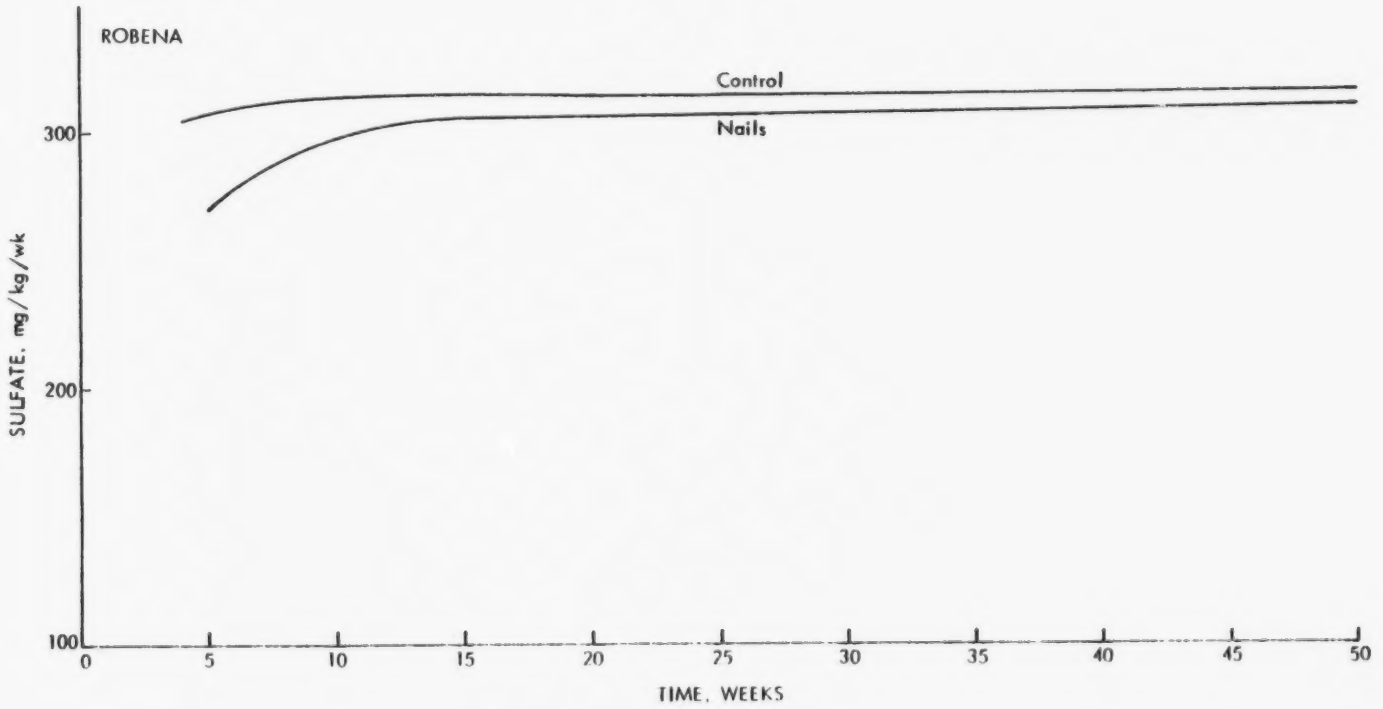


FIGURE 18. - Sulfate versus time plots: Robena pyrite.

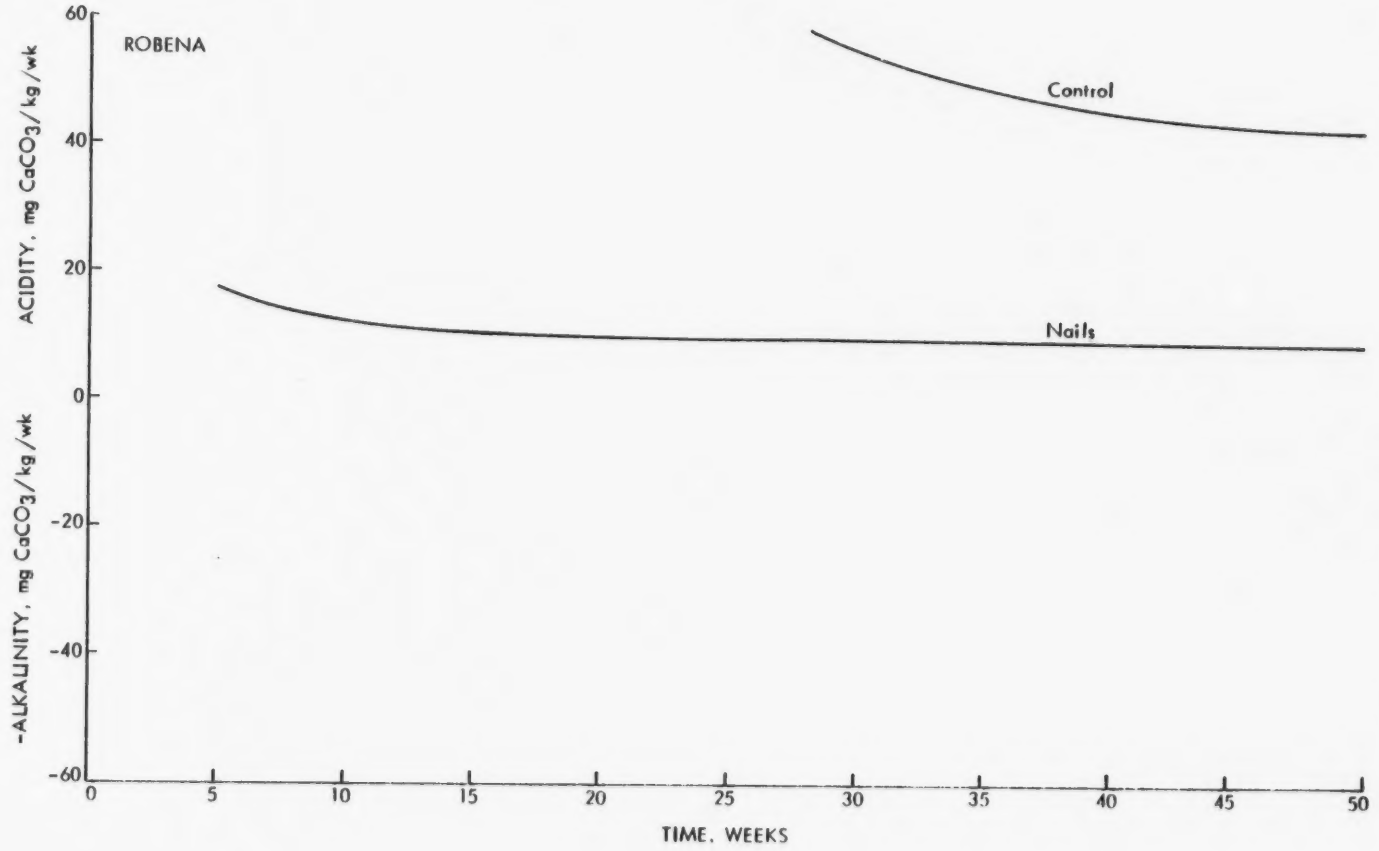
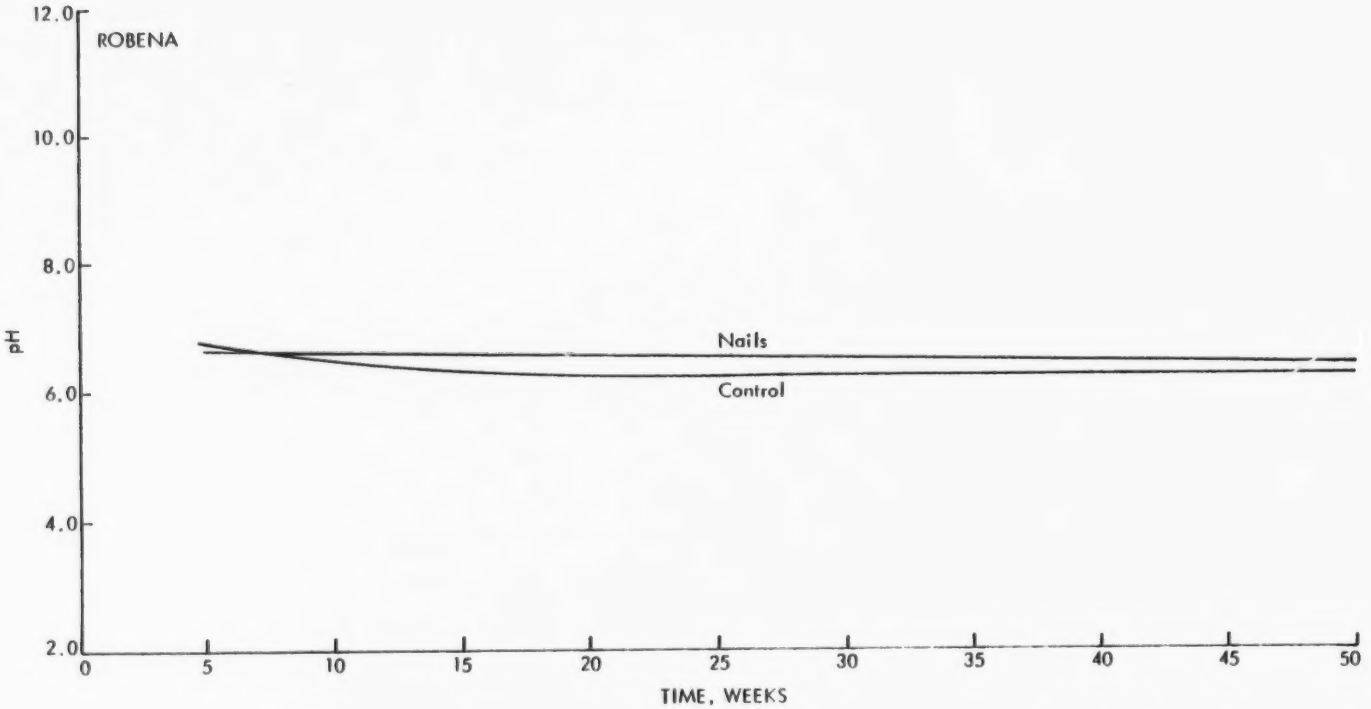


FIGURE 19. - Acidity versus time plots: Robena pyrite.



FIGUR E 20. - pH versus time plots: Robena pyrite.

The averages and standard deviation of the various parameters in the two Robena experiments have been established, along with the correlation between the individual parameters. These results are shown in Table 11 (Robena control) and Table 12 (Robena nail-inhibited). Unlike the results with Valley Camp No. 1, constituents determined from the untreated Robena pyrite do not correlate with one another. A weak correlation is observed between ferrous and total iron.

On the other hand, weak correlation between total iron and sulfate, acidity, and pH are noted for the iron nail-inhibited Robena experiment (Table 12). These correlations between total iron and sulfate and acid, although not as strong as those observed for Valley Camp No. 1 (Table 4), do suggest that ferric iron (total iron less ferrous iron) has some effect on acid mine drainage formation. The very strong correlation between pH and acidity in the Robena nail system is believed to be fortuitous.

The averages and standard deviation of the two Robena experiments have been analyzed statistically using the procedures described for Valley Camp No. 1 pyrite. Results are shown in Table 13. It is seen that there is no significant difference between all the constituents except for iron II. Here, the difference is almost nonsignificant, the "t" value at the 95% confidence level and 24 degrees of freedom being 2.06.

Thus, we conclude that little difference is present between the untreated and iron nail-inhibited Robena pyrite.

Maple Creek Pyrite

Results from the Maple Creek pyrite experiments from data presented in Appendix C were subjected to an identical analysis. One control experiment and three inhibitor (iron nails, fly ash, and slag) experiments were conducted with Maple Creek pyrite. The regression equations fitting these data to hyperbolic curves are shown in Table 14, and constituent-time plots are shown in Figures 21 through 25:

* Figure 21 - Iron II versus time: Maple Creek pyrite,
* Figure 22 - Iron total versus time: Maple Creek pyrite,
* Figure 23 - Sulfate versus time: Maple Creek pyrite,
* Figure 24 - Acidity versus time: Maple Creek pyrite, and
* Figure 25 - pH versus time: Maple Creek pyrite.

TABLE 11. - Average values, standard deviations, and correlation coefficients between parameters: Robena - control (N = 13)

	Iron II	Iron total	Sulfate	Acidity[a/]	pH
Iron II	AV = 0.01 mg/kg/wk SD = ± 0.01 mg/kg/wk	r = 0.585 *	r = 0.059 NS	r = 0.210 NS	r = -0.298 NS
Iron total		AV = 0.30 mg/kg/wk SD = ± 0.66 mg/kg/wk	r = 0.183 NS	r = 0.120 NS	r = -0.388 NS
Sulfate			AV = 309 mg/kg/wk SD = ± 52 mg/kg/wk	r = -0.058 NS	r = -0.561 *
Acidity[a/]				AV = -16 mg/kg/wk SD = ± 13 mg/kg/wk	r = -0.530 NS
pH					AV = 7.1 SD = ± 0.9

a/ Alkalinity = - acidity.
* Significant at 95% confidence level.
NS = Not significant at 95% confidence level.

TABLE 12. - Average values, standard deviations, and correlation coefficients between parameters: Robena - iron nails (N = 13)

	Iron II	Iron total	Sulfate	Acidity[a/]	pH
Iron II	AV = 0.002 mg/kg/wk SD = ± 0.008 mg/kg/wk	r = -0.148 NS	r = 0.389 NS	r = 0.377 NS	r = -0.328 NS
Iron total		AV = 0.044 mg/kg/wk SD = ± 0.048 mg/kg/wk	r = -0.598 *	r = -0.650 *	r = 0.675 *
Sulfate			AV = 310 mg/kg/wk SD = ± 61 mg/kg/wk	r = 0.474 NS	r = -0.586 *
Acidity[a/]				AV = -8 mg/kg/wk SD = ± 16 mg/kg/wk	r = -0.966 ***
pH					AV = 7.1 SD = ± 0.9

a/ Alkalinity = - acidity.
*** Significant at 95% level.
* Significant at 99.9% level.
NS = Not significant at 95% level.

TABLE 13. - Statistical comparison of averages by inhibitor: Robena pyrite

System: Control/Iron nails ($n_c + n_n - 2 = 24$)

Iron II:	$Av_c = 0.01$;	$Av_n = 0.002$;	$t = 2.12$;	*
Iron total:	$Av_c = 0.30$;	$Av_n = 0.044$;	$t = 1.40$;	NS
Sulfate:	$Av_c = 309$;	$Av_n = 310$;	$t = 0.03$;	NS
Acidity:	$Av_c = -16$;	$Av_n = -8$;	$t = 1.32$;	NS
pH:	$Av_c = 7.1$;	$Av_n = 7.1$;	$t = 0.06$;	NS

* Significant at 95% confidence level.
Subscript $_c$ = control
Subscript $_n$ = iron nails
Subscript $_t$ = "Student" t
NS = Not significant at 95% confidence total.

TABLE 14. - Regression equations relating generation of pyrite oxidation products with time: Maple Creek pyrite

Control (N = 25)		
y = Iron II (mg/kg)	x/y = 1575.860 + 105.311x	r = 0.145
y = Iron Total (mg/kg)	x/y = -19.870 + 12.530x	r = 0.601
y = Sulfate (mg/kg)	x/y = -0.002 + 0.004x	r = 0.959
y = Acidity (mg $CaCO_3$/kg)	x/y = 0.275 - 0.072x	r = 0.799
y = pH	x/y = -0.100 + 0.153x	r = 0.987
Nail Inhibited (N = 14)		
y = Iron II (mg/kg)	x/y = -6003.295 + 1086.551x	r = 0.703
y = Iron Total (mg/kg)	x/y = -46.535 + 9.221x	r = 0.654
y = Sulfate (mg/kg)	x/y = -0.012 + 0.005x	r = 0.937
y = Acidity (mg $CaCO_3$/kg)	x/y = 1.852 - 0.224x	r = -0.405
y = pH	x/y = 0.199 + 0.125x	r = 0.968
Fly Ash Inhibited (N = 14)		
y = Iron II (mg/kg)	x/y = -1930.070 + 986.626x	r = 0.706
y = Iron Total (mg/kg)	x/y = 6.613 + 19.466x	r = 0.794
y = Sulfate (mg/kg)	x/y = -0.013 + 0.004x	r = 0.994
y = Acidity (mg $CaCO_3$/kg)	x/y = -0.435 - 0.010x	r = -0.183
y = pH	x/y = 0.087 + 0.122x	r = 0.995
Slag Inhibited (N = 25)		
y = Iron II (mg/kg)	x/y = -955.212 + 406.452x	r = 0.376
y = Iron Total (mg/kg)	x/y = 57.660 + 0.131x	r = 0.011
y = Sulfate (mg/kg)	x/y = -0.006 + 0.004x	r = 0.977
y = Acidity (mg $CaCO_3$/kg)	x/y = 0.701 - 0.149x	r = -0.565
y = pH	x/y = 0.119 + 0.169x	r = 0.985

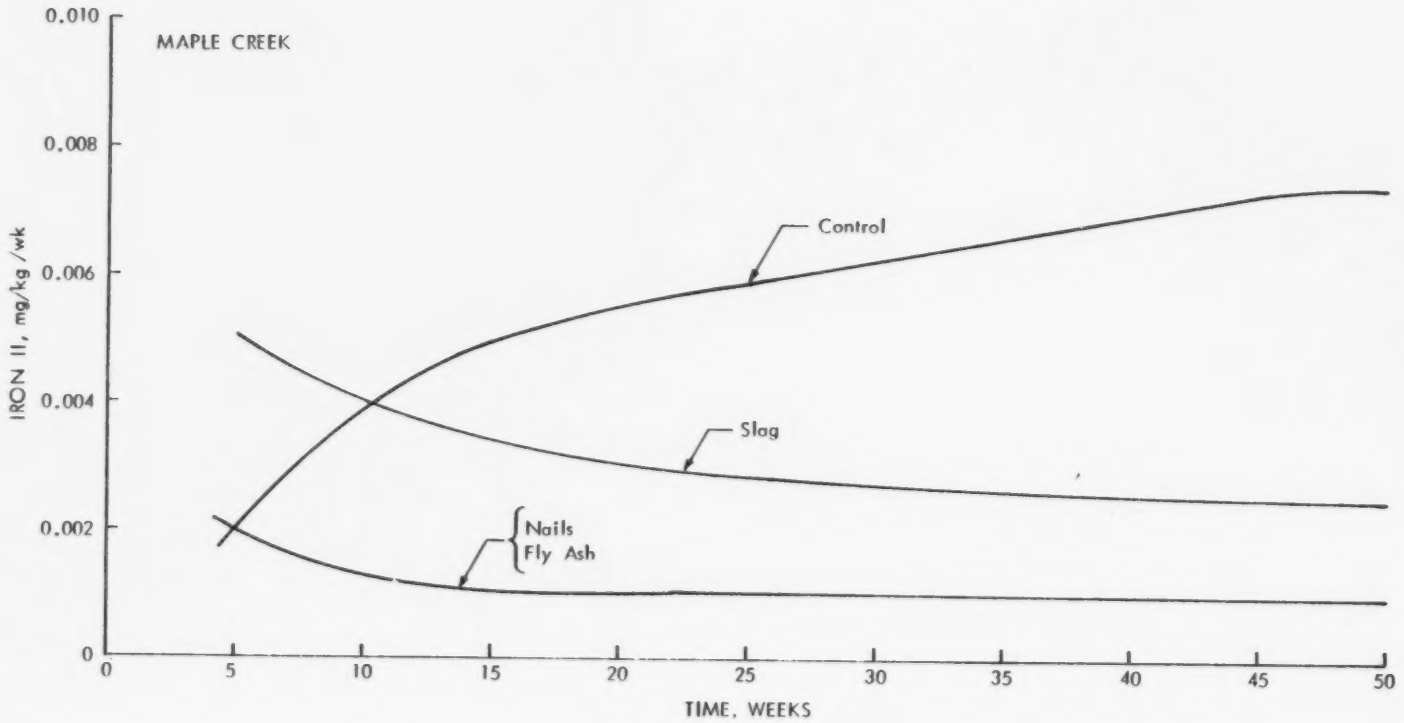


FIGURE 21. - Iron II - time plots: Maple Creek pyrite.

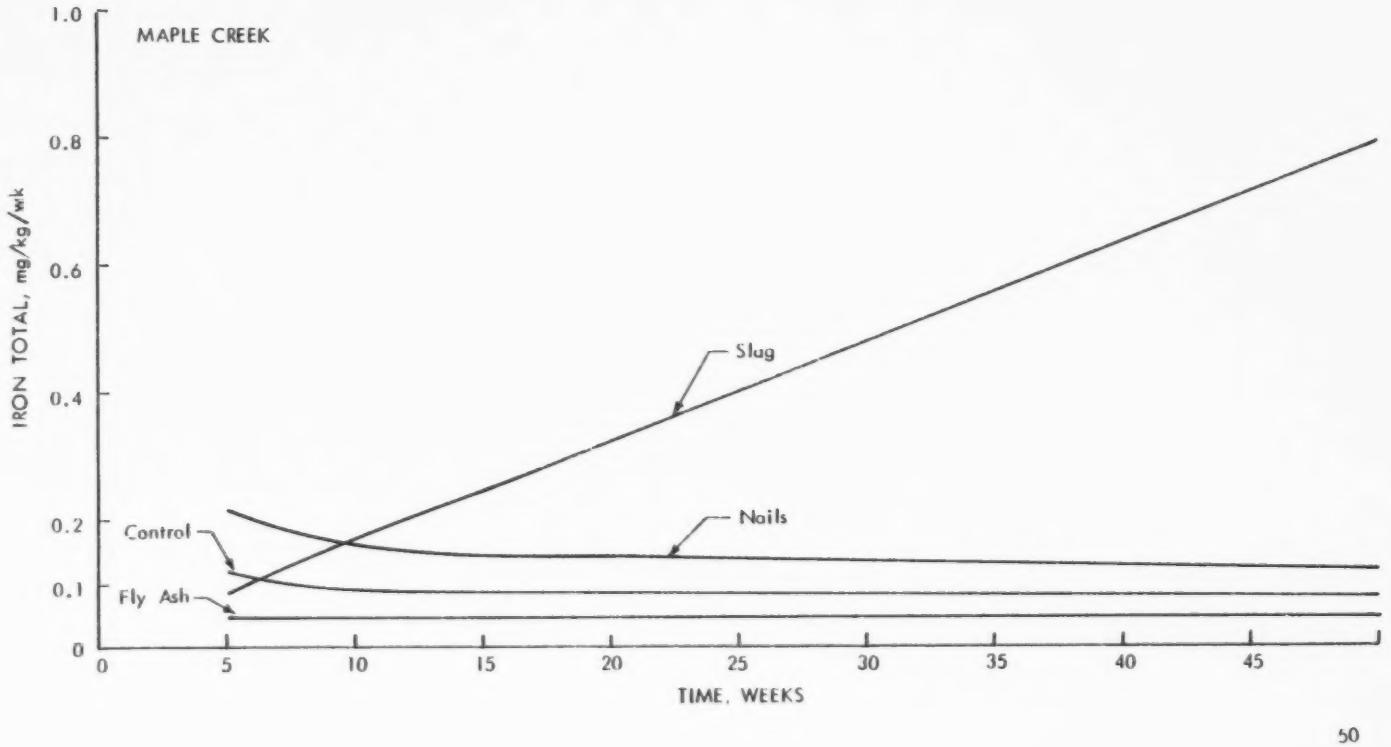


FIGURE 22. - Iron total - time plots: Maple Creek pyrite.

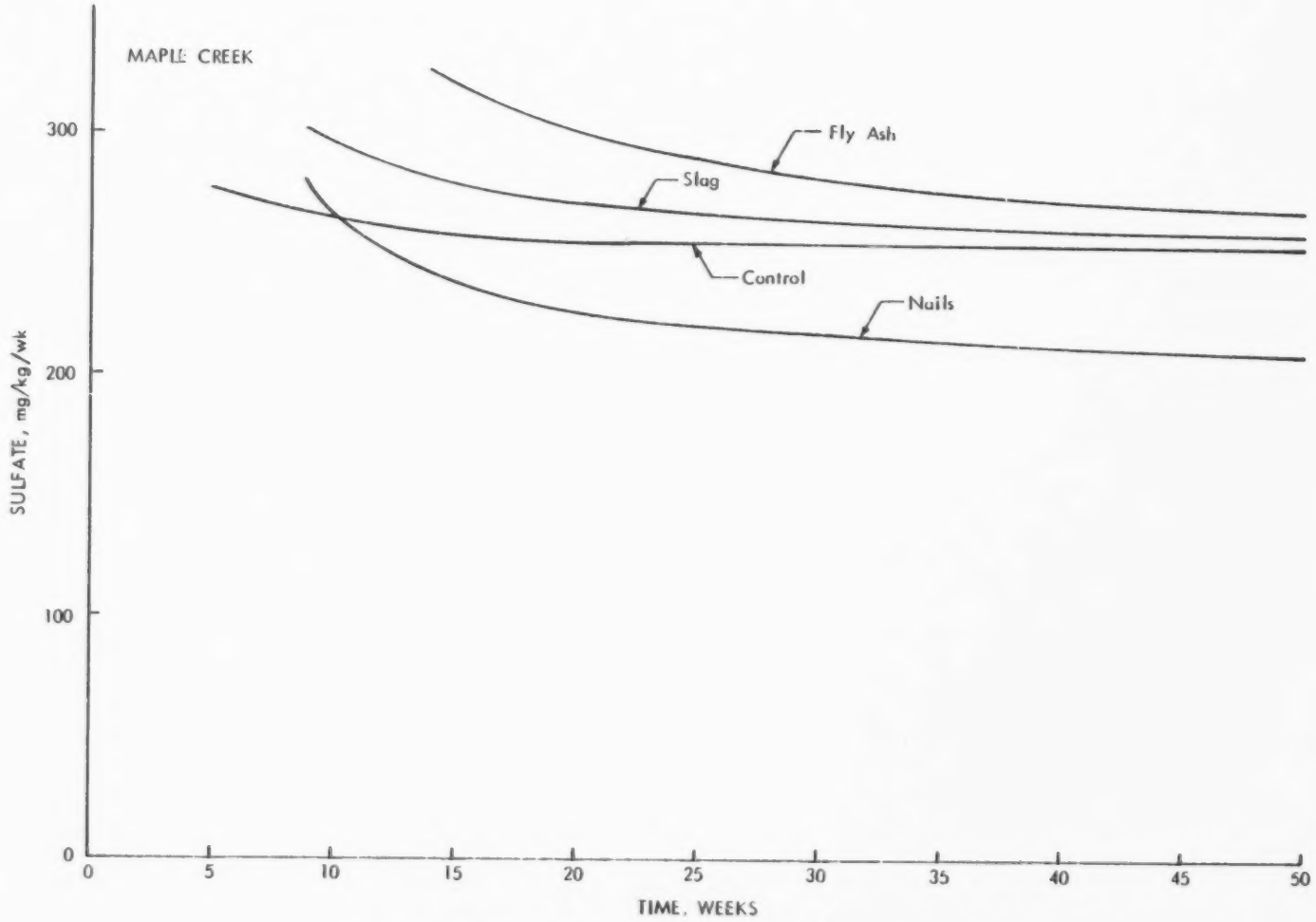


FIGURE 23. - Sulfate - time plots: Maple Creek pyrite.

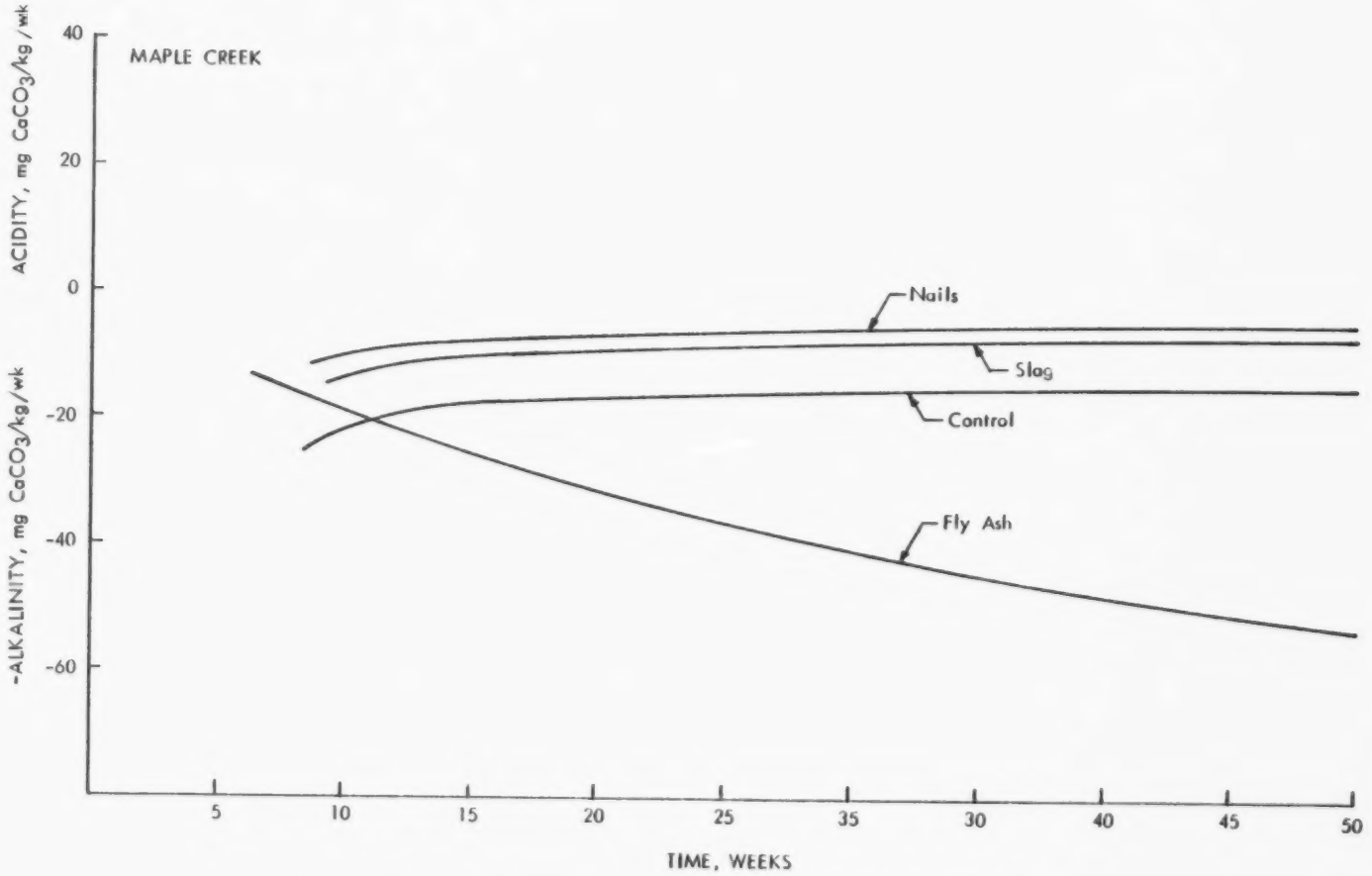


FIGURE 24. - Acidity - time plots: Maple Creek pyrite.

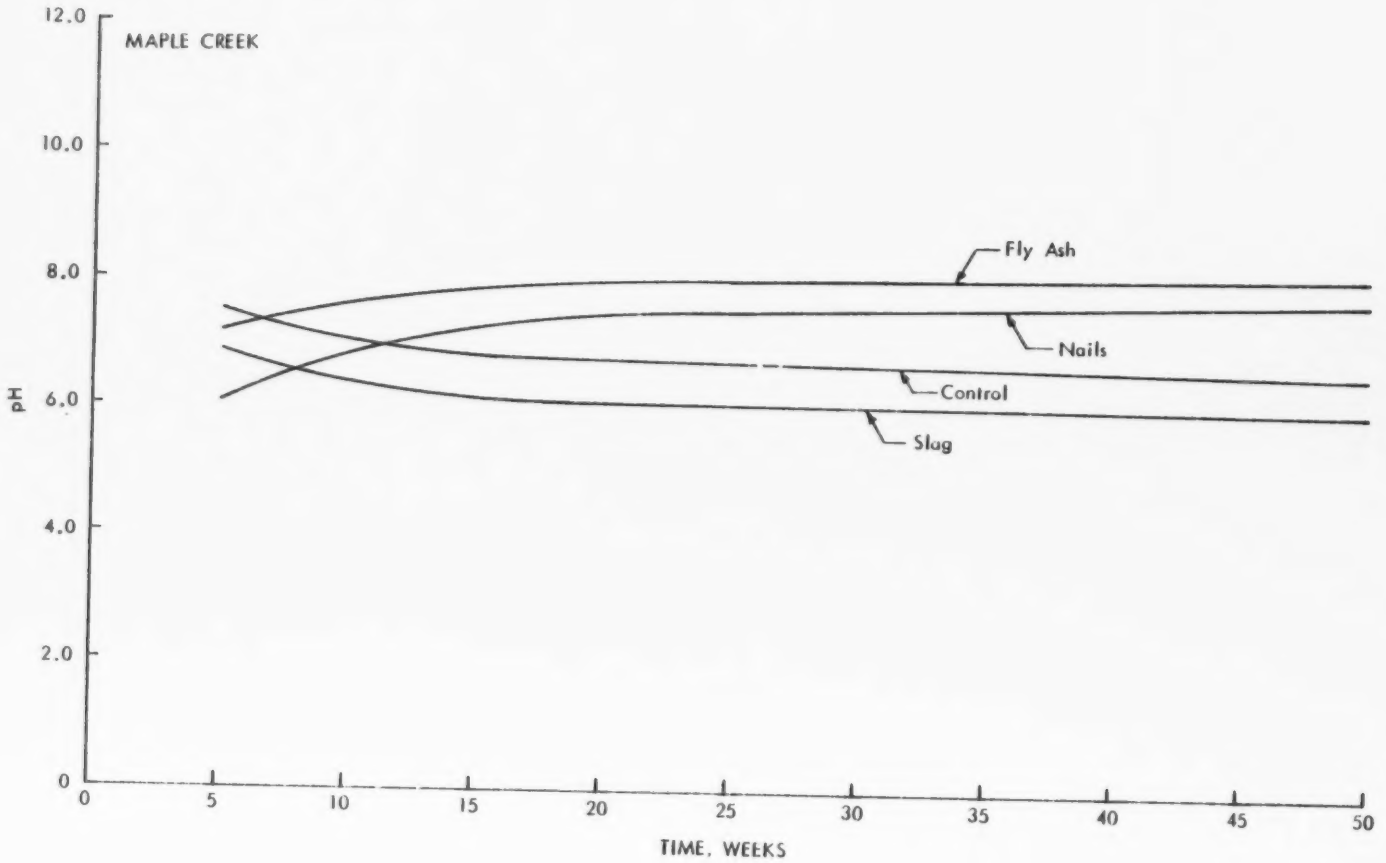


FIGURE 25. - pH - time plots: Maple Creek pyrite.

The plots for the Maple Creek systems show relatively small differences between the control and the three inhibited systems which is an indication that Maple Creek pyrite is not a pronounced generator of acid mine drainage.

The average values of each of the parameters and their standard deviation have been calculated, as have the correlation between constituent pairs. The results are shown in Tables 15 through 18 for the control experiment and the three inhibitors evaluated.

* Table 15 - Maple Creek: control,

* Table 16 - Maple Creek: iron nail-inhibited,

* Table 17 - Maple Creek: fly ash-inhibited, and

* Table 18 - Maple Creek: slag-inhibited.

The results for the Maple Creek systems indicate that stronger correlation exists in all four systems between constituent pairs than observed for Robena pyrite. These results suggest that the week-to-week variation in the Maple Creek studies were more consistent than they were in the Robena studies.

The average constituent levels observed for the Maple Creek control samples were very close to those observed for the Robena control. The averages obtained for the two pyrites in the several inhibited systems and in the untreated system are summarized in Figure 26. Here it can be seen that neither pyrite varies widely in the amount of material generated by the untreated pyrite.

On the other hand, the Maple Creek/nails system results in higher levels of ferrous iron, total iron, and acidity generated in the system. These data suggest that the nails are preferentially oxidized rather than pyrite to put more iron into the system. The sulfate levels in the Maple Creek/nail system are not different; hence, the nails are not really inhibiting, but rather serving as a source of iron other than pyrite in the system.

The high averages for sulfate in the Maple Creek/fly ash system are due to two results obtained from the sulfate analyses. The sulfate level for the system was 2,357 mg/kg in the 3rd week and 1,100 mg/kg in the 5th week. Inclusion of these two values in the analysis has yielded a high sulfate average for this system. However, when the values are included in the regression analysis with time, their influence on the results is much reduced as has been shown by the plot in Figure 23.

TABLE 15. - Average values, standard deviations, and correlation coefficients between parameters: Maple Creek - control (N = 23)

	Iron II	Iron total	Sulfate	Acidity[a/]	pH
Iron II	AV = 0.014 mg/kg/wk SD = ± 0.012 mg/kg/wk	r = 0.394 NS	r = 0.741 ***	r = 0.206 NS	r = -0.529 **
Iron total		AV = 0.44 mg/kg/wk SD = ± 0.87 mg/kg/wk	r = 0.506 *	r = 0.217 NS	r = -0.360 NS
Sulfate			AV = 316 mg/kg/wk SD = ± 168 mg/kg/wk	r = 0.034 NS	r = -0.379 NS
Acidity[a/]				AV = -23 mg/kg/wk SD = ± 8 mg/kg/wk	r = -0.358 NS
pH					AV = 6.9 SD = ± 0.6

a/ Alkalinity = - acidity.
*** Significant at 99.9% confidence level.
** Significant at 99% confidence level.
* Significant at 95% confidence level.
NS = Not significant at 95% confidence level.

TABLE 16. - Average values, standard deviations, and correlation coefficients between parameters: Maple Creek - iron nails (N = 12)

	Iron II	Iron total	Sulfate	Acidity[a/]	pH
Iron II	AV = 3.4 mg/kg/wk SD = ± 4.4 mg/kg/wk	r = 0.999 ***	r = 0.892 ***	r = 0.932 ***	r = -0.694 *
Iron total		AV = 3.9 mg/kg/wk SD = ± 4.4 mg/kg/wk	r = 0.875 ***	r = 0.929 ***	r = -0.684 *
Sulfate			AV = 348 mg/kg/wk SD = ± 211 mg/kg/wk	r = 0.742 *	r = -0.480 NS
Acidity[a/]				AV = 5 mg/kg/wk SD = ± 13 mg/kg/wk	r = -0.768 **
pH					AV = 6.6 SD = ± 0.8

a/ Alkalinity = - acidity.
*** Significant at 99.9% confidence level.
** Significant at 95% confidence level.
* Significant at 99% confidence level.
NS = Not significant at 95% confidence level.

TABLE 17. - Average values, standard deviations, and correlation coefficients between parameters: Maple Creek - fly ash (N = 12)

	Iron II	Iron total	Sulfate	Acidity[a/]	pH
Iron II	AV = 0.006 mg/kg/wk SD = ± 0.012 mg/kg/wk	r = 0.859 ***	r = 0.855 ***	r = 0.176 NS	r = -0.571 NS
Iron total		AV = 0.067 mg/kg/wk SD = ± 0.058 mg/kg/wk	r = 0.803 ***	r = 0.107 NS	r = -0.504 NS
Sulfate			AV = 652 mg/kg/wk SD = ± 587 mg/kg/wk	r = 0.503 NS	r = -0.862 ***
Acidity[a/]				AV = -17 mg/kg/wk SD = ± 6 mg/kg/wk	r = -0.651 *
pH					AV = 7.4 SD = ± 0.6

a/ Alkalinity = - acidity.
*** Significant at 99.9% confidence level.
* Significant at 95% confidence level.
NS Not significant at 95% confidence level.

TABLE 18. - Average values, standard deviations, and correlation coefficients between parameters: Maple Creek - slag (N = 23)

	Iron II	Iron total	Sulfate	Acidity[a/]	pH
Iron II	AV = 0.18 mg/kg/wk SD = ± 0.51 mg/kg/wk	r = 0.682 ***	r = 0.884 ***	r = 0.530 **	r = -0.464 *
Iron total		AV = 0.87 mg/kg/wk SD = ± 0.87 mg/kg/wk	r = 0.595 **	r = 0.289 NS	r = -0.399 NS
Sulfate			AV = 351 mg/kg/wk SD = ± 181 mg/kg/wk	r = 0.393 NS	r = -0.343 NS
Acidity[a/]				AV = -14 mg/kg/wk SD = ± 10 mg/kg/wk	r = -0.622 **
pH					AV = 6.3 SD = ± 0.6

a/ Alkalinity = - acidity.
*** Significant at 99.9% confidence level.
** Significant at 99% confidence level.
* Significant at 95% confidence level.

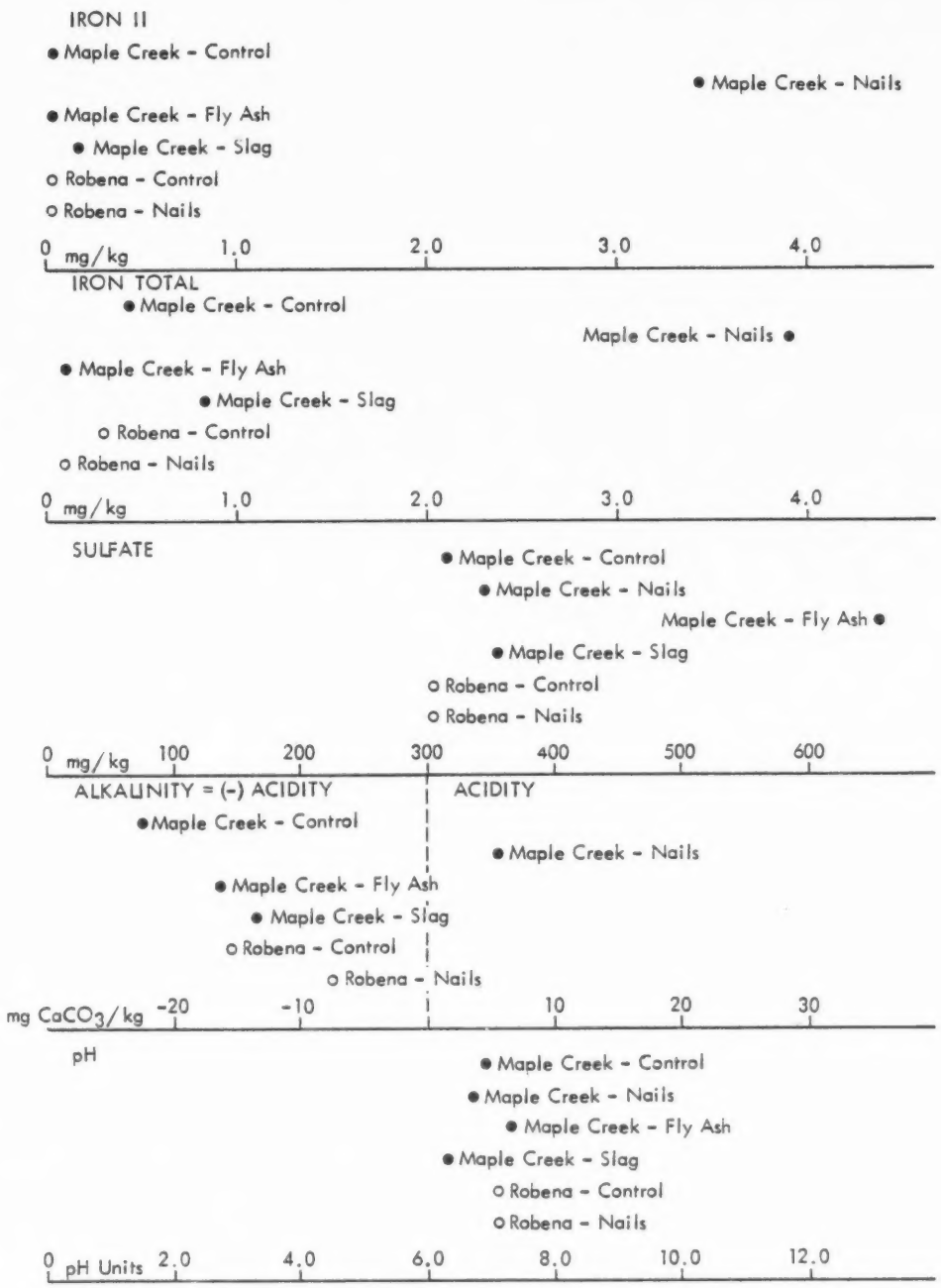

IRON II
● Maple Creek - Control
● Maple Creek - Nails
● Maple Creek - Fly Ash
● Maple Creek - Slag
o Robena - Control
o Robena - Nails
0 mg/kg 1.0 2.0 3.0 4.0
IRON TOTAL
● Maple Creek - Control
Maple Creek - Nails ●
● Maple Creek - Fly Ash
● Maple Creek - Slag
o Robena - Control
o Robena - Nails
0 mg/kg 1.0 2.0 3.0 4.0
SULFATE
● Maple Creek - Control
● Maple Creek - Nails
Maple Creek - Fly Ash ●
● Maple Creek - Slag
o Robena - Control
o Robena - Nails
0 mg/kg 100 200 300 400 500 600
ALKALINITY = (-) ACIDITY
ACIDITY
● Maple Creek - Control
● Maple Creek - Nails
● Maple Creek - Fly Ash
● Maple Creek - Slag
o Robena - Control
o Robena - Nails
mg $CaCO_3$/kg -20 -10 10 20 30
pH
● Maple Creek - Control
● Maple Creek - Nails
● Maple Creek - Fly Ash
● Maple Creek - Slag
o Robena - Control
o Robena - Nails
0 pH Units 2.0 4.0 6.0 8.0 10.0 12.0

FIGURE 26. - Summary of average values: Robena and Maple Creek pyrites.

Statistical comparison of the constituent averages between various pairs of untreated and inhibited Maple Creek systems are shown in Table 19. The averages are statistically different in a number of cases. However, they are not as different as those observed with the Valley Camp No. 1 pyrite (Table 9). Thus, even though the averages may be statistically different for the Maple Creek experiments, the magnitude of the differences are small enough to find the pyrite to be essentially a low producer of acid mine drainage.

TABLE 19. - Statistical comparison of averages by inhibitor: Maple Creek pyrite

System:	Control/Iron Nails ($n_c + n_n - 2 = 33$)					
Iron II:	Av_c = 0.014;	Av_n =	3.4;	t =	3.77;	***
Iron Total:	Av_c = 0.44;	Av_n =	3.9;	t =	3.67;	***
Sulfate:	Av_c = 316;	Av_n =	348;	t =	0.48;	NS
Acidity:	Av_c = - 23;	Av_n =	5;	t =	8.41;	***
pH:	Av_c = 6.9;	Av_n =	6.6;	t =	1.27;	NS
System:	Control/Fly Ash ($n_c + n_f - 2 = 33$)					
Iron II:	Av_c = 0.014;	Av_f =	0.006;	t =	1.89;	NS
Iron Total:	Av_c = 0.44;	Av_f =	0.067;	t =	2.09;	*
Sulfate:	Av_c = 316;	Av_f =	653;	t =	2.53;	*
Acidity:	Av_c = - 23;	Av_f =	- 17;	t =	2.48;	*
pH:	Av_c = 6.9;	Av_f =	7.4;	t =	2.59;	*
System:	Control/Slag ($n_c + n_s - 2 = 44$)					
Iron II:	Av_c = 0.014;	Av_s =	0.18;	t =	1.52;	NS
Iron Total:	Av_c = 0.44;	Av_s =	0.87;	t =	1.66;	NS
Sulfate:	Av_c = 316;	Av_s =	653;	t =	0.49;	NS
Acidity:	Av_c = - 23;	Av_s =	- 14;	t =	3.58;	***
pH:	Av_c = 6.9;	Av_s =	6.3;	t =	3.47;	**
System:	Iron Nails/Fly Ash ($n_n + n_f - 2 = 22$)					
Iron II:	Av_n = 3.4;	Av_f =	0.006;	t =	2.69;	*
Iron Total:	Av_n = 3.9;	Av_f =	0.067;	t =	5.33;	***
Sulfate:	Av_n = 348;	Av_f =	653;	t =	1.66;	NS
Acidity:	Av_n = 5;	Av_f =	- 17;	t =	4.20;	***
pH:	Av_n = 6.6;	Av_f =	7.4;	t =	2.87;	**
System:	Iron Nails/Slag ($n_n + n_s - 2 = 33$)					
Iron II:	Av_n = 3.4;	Av_s =	0.18;	t =	3.54;	***
Iron Total:	Av_n = 3.9;	Av_s =	0.87;	t =	3.22;	**
Sulfate:	Av_n = 348;	Av_s =	351;	t =	0.06;	NS

TABLE 19. - Statistical comparison of averages by inhibitor: Maple Creek pyrite - Continued

Acidity:	Av_n =	5;	Av_s =	- 14;	t =	5.14;	***
pH:	Av_n =	6.6;	Av_s =	6.3;	t =	1.30;	NS
System:	Fly Ash/Slag ($n_f + n_s - 2 = 33$)						
Iron II:	Av_f =	0.006;	Av_s =	0.18;	t =	1.15;	NS
Iron Total:	Av_f =	0.067;	Av_s =	0.87;	t =	3.17;	**
Sulfate:	Av_f =	653;	Av_s =	351;	t =	2.24;	*
Acidity:	Av_f =	- 17;	Av_s =	- 14;	t =	0.96;	NS
pH:	Av_f =	7.4;	Av_s =	6.3;	t =	5.14;	***

Subscript c = Control
Subscript n = Iron nails
Subscript f = Fly ash
Subscript s = Slag
t = "Student" t
*** Significant at 99.9% confidence level.
** Significant at 99% confidence level.
* Significant at 95% confidence level.
NS Not significant at 95% confidence level.

COMPARISON OF EXPERIMENTAL RESULTS AMONG PYRITES

The discussion to this point has dealt with the effects of inhibition of acid mine drainage formation on the individual pyrites. We shall now address the question of differences among the pyrites as reflected by their response to different inhibitor treatments.

The responses of the pyrites to the different treatments are summarized in Figures 27 through 31 for the several components of acid mine drainage:

* Figure 27 - Iron II,

* Figure 28 - Iron total,

* Figure 29 - Sulfate,

* Figure 30 - Acidity, and

* Figure 31 - pH.

The comparison of iron II results in Figure 27 show clearly that the Valley Camp No. 1 pyrite is the greatest producer of ferrous iron in the untreated state. In the presence of iron nails, the iron II levels of both Valley Camp No. 1 and Maple Creek increase slightly. However, when the pyrites are treated with fly ash, slag, portland cement, or kiln dust, levels of ferrous iron drop to nearly zero. Thus, we can conclude that iron II formation is inhibited by treatments with alkaline materials but that it may increase in the presence of metallic iron.

The pattern observed with the total iron values (Figure 28) is similar to that of iron II. The generation of total iron is inhibited by the presence of the alkaline materials--fly ash, slag, portland cement, and kiln dust. A decrease in total iron is noted when the strongly acid-producing Valley Camp No. 1 pyrite is inhibited with nails. The Valley Camp case implies that the ferrous-ferric ratio in the iron nail-treated system is greater than that of the untreated system and suggests that keeping iron in the ferrous state tends to reduce overall oxidation of pyrite.

The reduction of pyrite oxidation in the presence of metallic iron is seen further in the sulfate results. The sulfate levels (Figure 29) in the nail-treated Valley Camp pyrite is about 70% of that in the control sample.

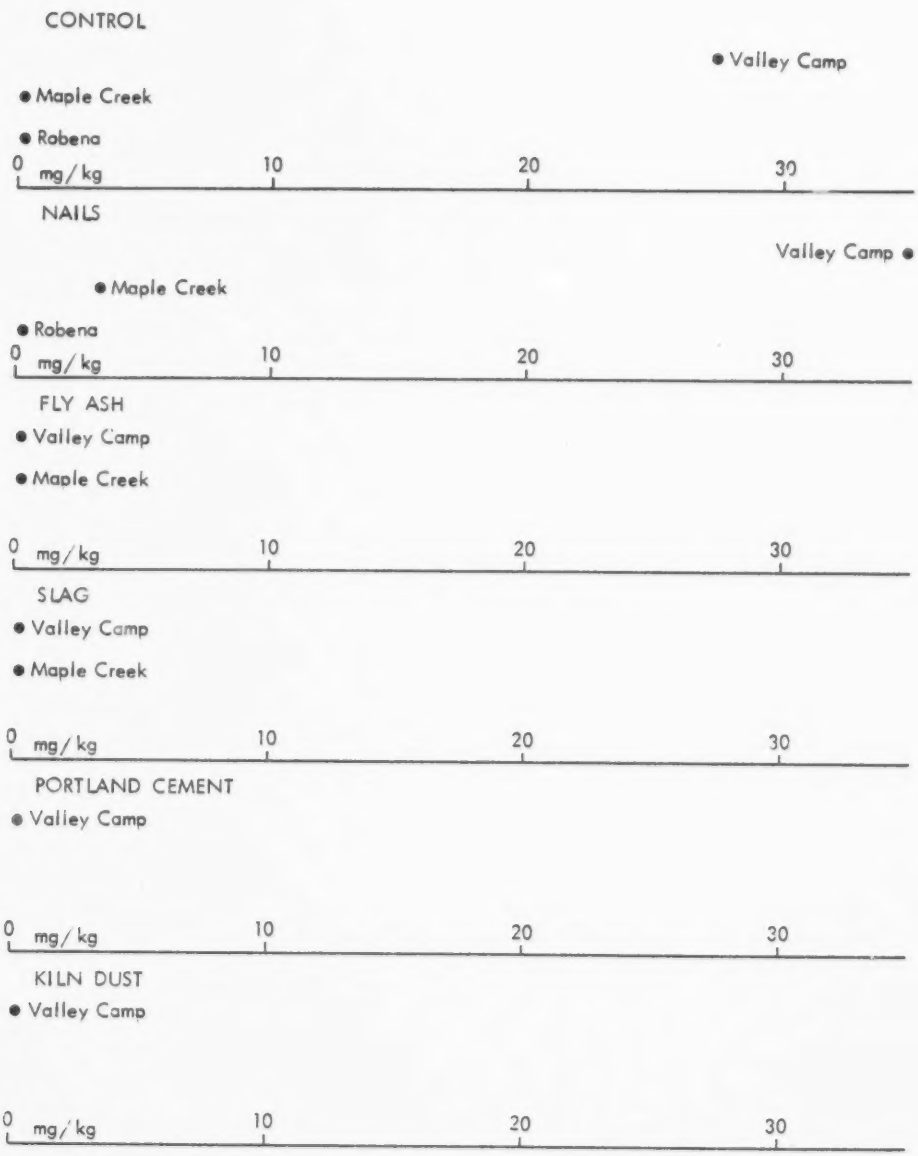


FIGURE 27. - Summary of iron II results for all pyrites.

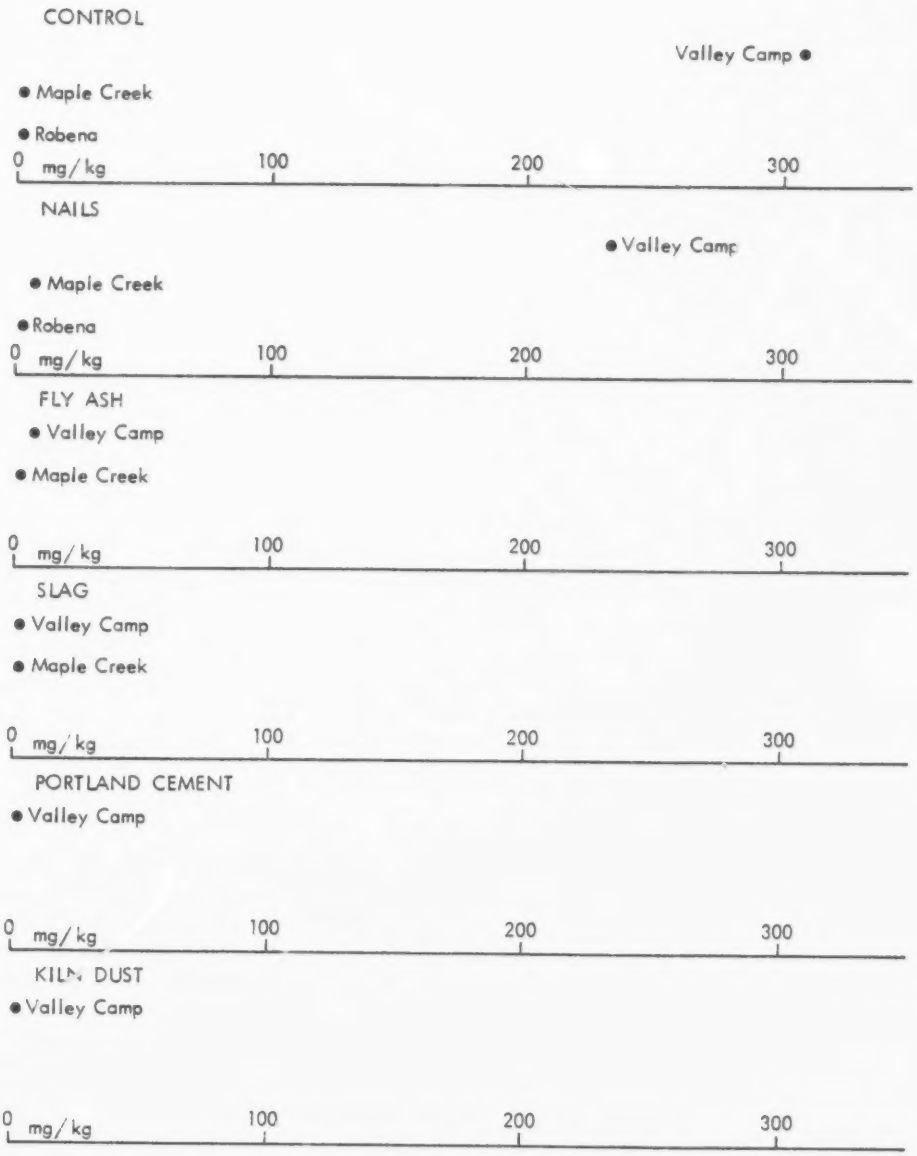


FIGURE 28. - Summary of total iron results for all pyrites.

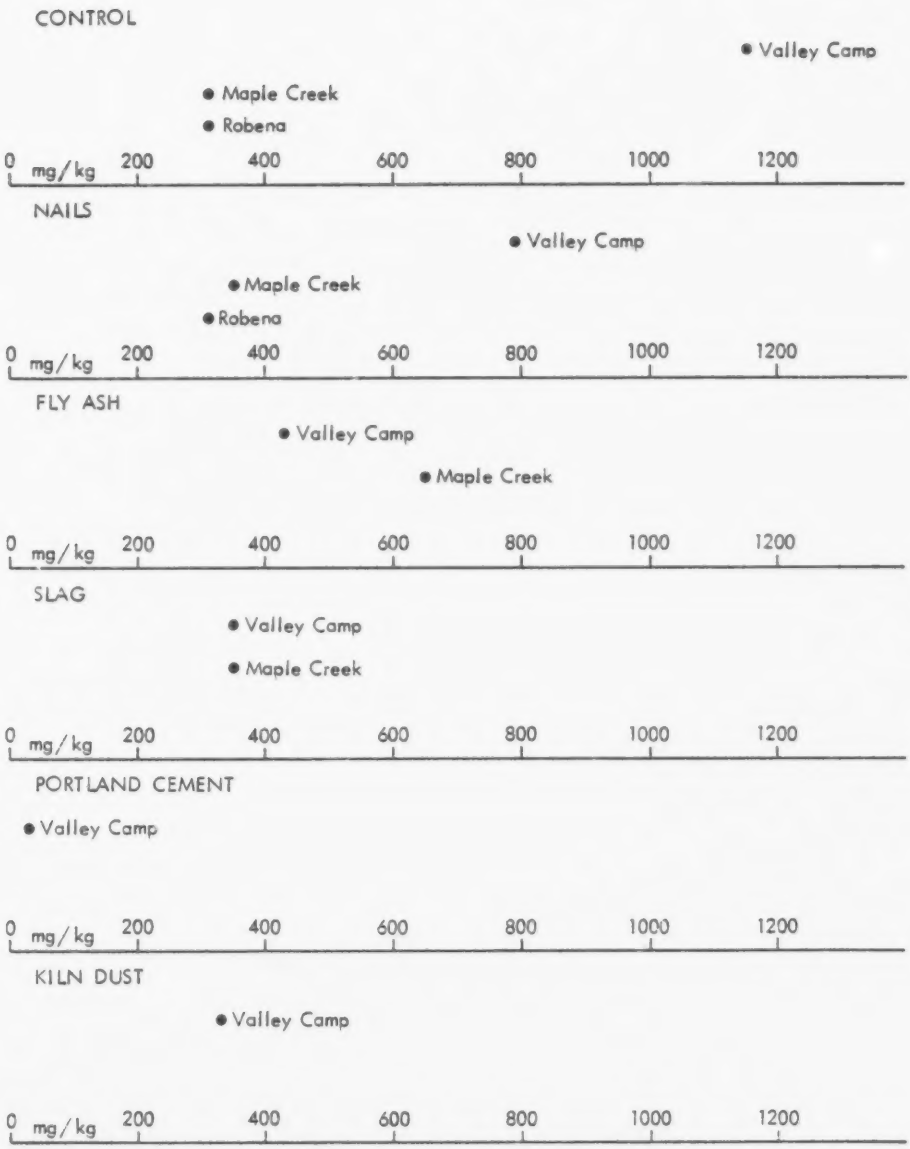


FIGURE 29. - Summary of sulfate results for all pyrites.

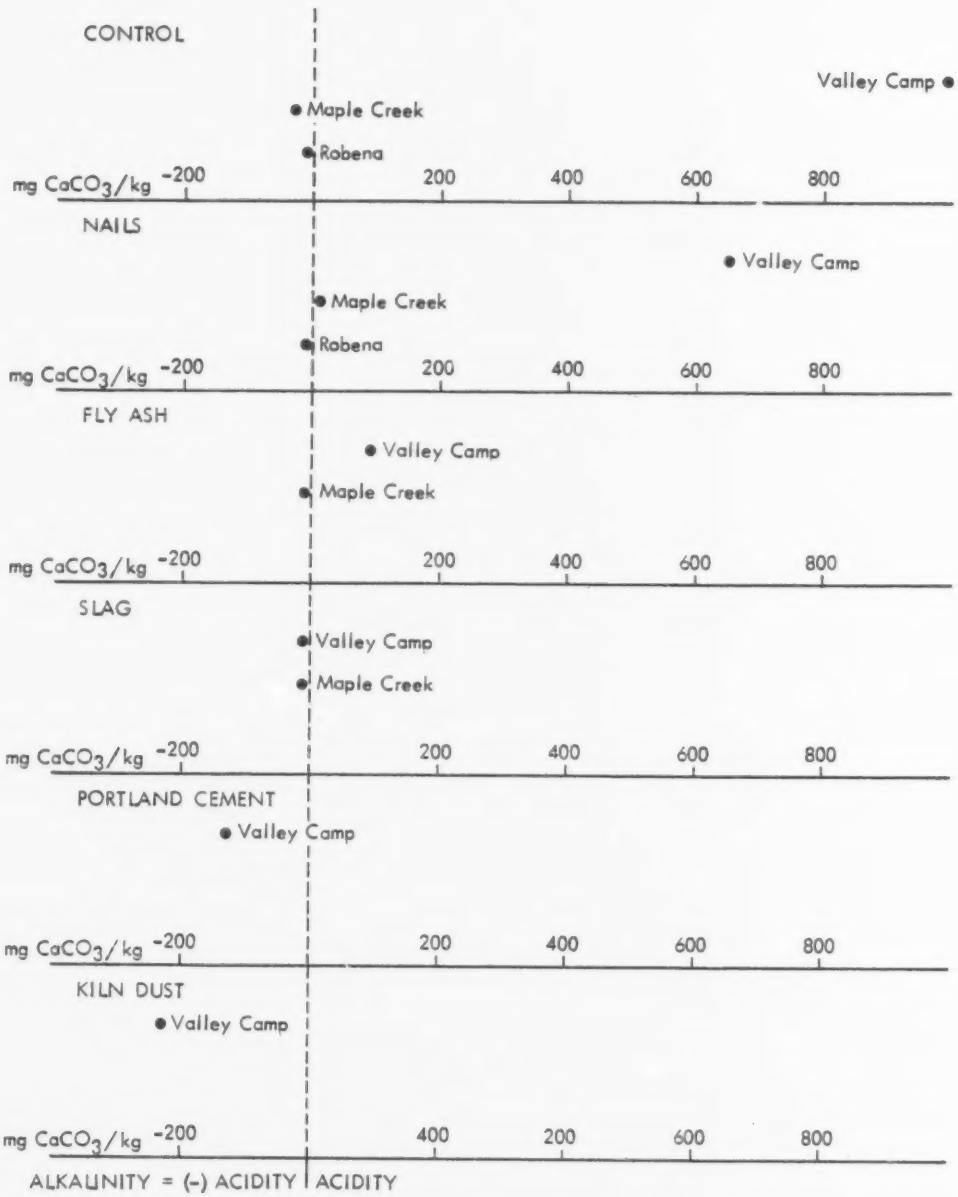


FIGURE 30. - Summary of acidity results for all pyrites.

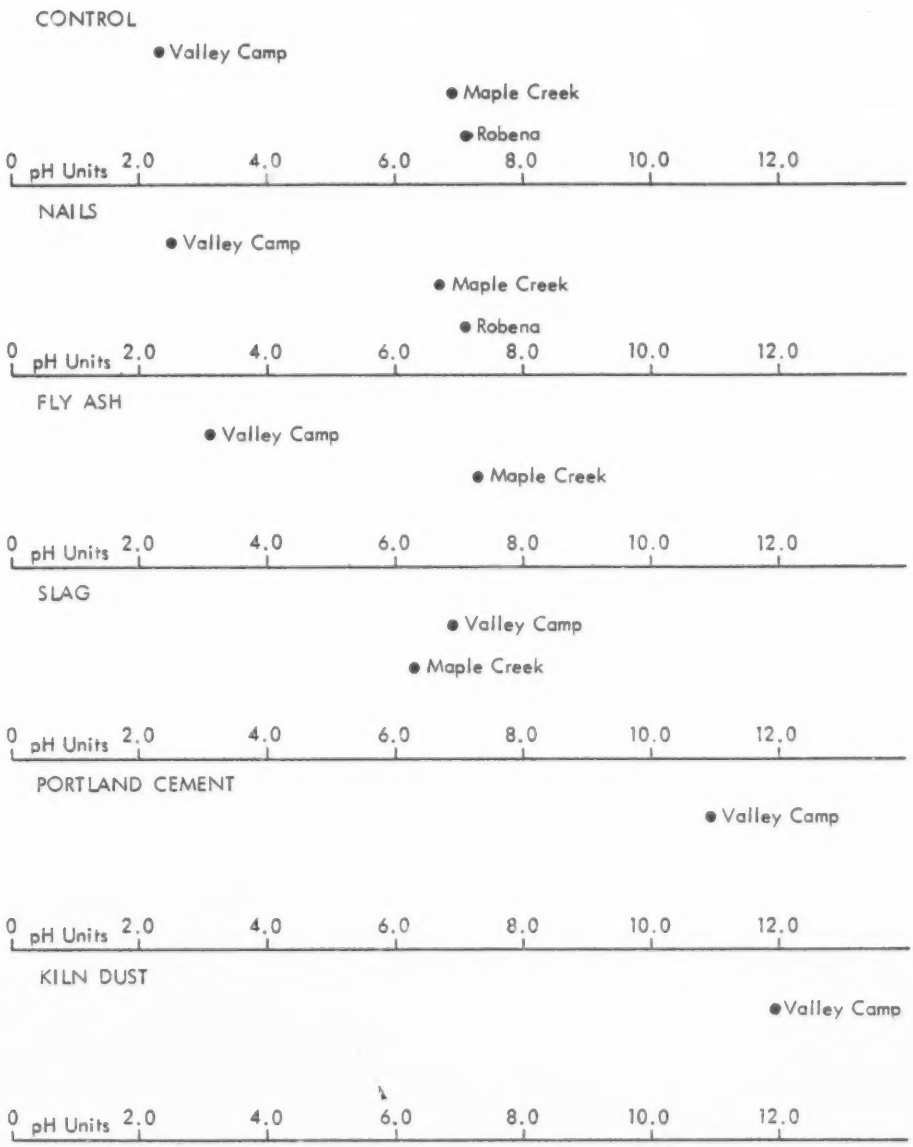


FIGURE 31. - Summary of pH results for all pyrites.

Thus, the decrease in total iron corresponds with a decrease in sulfate. When these observations are coupled with that of increased iron II levels for the Valley Camp system, one can conclude that the metallic iron is oxidizing preferentially to pyrite and behaves as a sacrificial electrode.

A minor increase in sulfate is noted for the Maple Creek systems. However, as shown in Table 19, the difference in sulfate levels between the control and nail-treated experiment are not significant in the statistical sense. Thus, it appears that the metallic iron can reduce pyrite oxidation in the systems which are acid mine drainage producing but has little effect on those which are not.

When the Valley Camp pyrite is subjected to treatment with fly ash, slag, portland cement, or kiln dust, sulfate levels drop even further, suggesting pronounced inhibition of pyrite oxidation in these systems. The increased sulfate level observed in the fly ash-treated Maple Creek system is not understood, and may be an anomaly because of the presence of two excessively large values in the raw data.

The plot of acidity in Figure 30 clearly shows the differences among the three pyrites in their ability to generate acid--Valley Camp No. 1 is acid-producing whereas Robena and Maple Creek are essentially neutral. Acid production can be reduced by all of the treatments for Valley Camp. Acid production is affected little by treatment of Robena and Maple Creek pyrites. When the Valley Camp No. 1 pyrite is treated with portland cement or cement kiln dust, one tends to trade acidity for alkalinity. However, alkalinity values are lower than acidity levels in the untreated pyrite.

The last figure summarizes pH results (Figure 31). Here again, we can see that the Valley Camp No. 1 pyrite is acid-producing, whereas the Robena and Maple Creek pyrites are essentially neutral. Inhibitor treatment of Valley Camp No. 1 pyrite will raise pH to levels corresponding to natural pHs of the inhibitor systems.

Differences among the pyrites have also been examined statistically using average values, and results are presented in Table 20. Here it can be seen that Valley Camp No. 1 pyrite is indeed different than either Robena or Maple Creek pyrites, and that differences among the various conditions using the same inhibitor are significant. Robena and Maple Creek pyrites do not appear to be different in the untreated state, although average results tend to differ significantly when both are treated with metallic iron.

TABLE 20. - Statistical comparison of averages by pyrite

Inhibitor - None (control)

Valley Camp/Robena ($n_{vc} + n_r - 2 = 39$)

Iron II:	Av_{vc} = 27;	Av_r = 0.01;	t = 2.18;	*
Iron Total:	Av_{vc} = 307;	Av_r = 0.30;	t = 8.25;	***
Sulfate:	Av_{vc} = 1,147;	Av_r = 309;	t = 23.20;	***
Acidity:	Av_{vc} = 986;	Av_r = -15;	t = 8.20;	***
pH:	Av_{vc} = 2.4;	Av_r = 7.1;	t = 26.35;	***

Valley Camp/Maple Creek ($n_{vc} + n_{mc} - 2 = 49$)

Iron II:	Av_{vc} = 27;	Av_{mc} = 0.014;	t = 3.12;	**
Iron Total:	Av_{vc} = 307;	Av_{mc} = 0.44;	t = 5.27;	***
Sulfate:	Av_{vc} = 1,147;	Av_{mc} = 316;	t = 20.27;	***
Acidity:	Av_{vc} = 986;	Av_{mc} = -23;	t = 11.05;	***
pH:	Av_{vc} = 2.4;	Av_{mc} = 6.9;	t = 39.83;	***

Robena/Maple Creek ($n_r + n_{mc} - 2 = 34$)

Iron II:	Av_r = 0.01;	Av_{mc} = 0.014;	t = 0.99;	NS
Iron Total:	Av_r = 0.30;	Av_{mc} = 0.44;	t = 0.50;	NS
Sulfate:	Av_r = 309;	Av_{mc} = 316;	t = 0.15;	NS
Acidity:	Av_r = -15;	Av_{mc} = -23;	t = 2.30;	*
pH:	Av_r = 7.1;	Av_{mc} = 6.9;	t = 1.12;	NS

Inhibitor - Iron Nails

Valley Camp/Robena ($n_{vc} + n_r - 2 = 39$)

Iron II:	Av_{vc} = 36;	Av_r = 0.002;	t = 2.82;	**
Iron Total:	Av_{vc} = 234;	Av_r = 0.044;	t = 7.61;	***
Sulfate:	Av_{vc} = 797;	Av_r = 310;	t = 7.58;	***
Acidity:	Av_{vc} = 644;	Av_r = -8;	t = 22.46;	***
pH:	Av_{vc} = 2.6;	Av_r = 7.1;	t = 55.62;	***

Valley Camp/Maple Creek ($n_{vc} + n_{mc} - 2 = 38$)

Iron II:	Av_{vc} = 36;	Av_{mc} = 3.4;	t = 2.45;	*
Iron Total:	Av_{vc} = 234;	Av_{mc} = 3.9;	t = 7.18;	***
Sulfate:	Av_{vc} = 797;	Av_{mc} = 348;	t = 5.86;	***
Acidity:	Av_{vc} = 644;	Av_{mc} = 5;	t = 21.17;	***
pH:	Av_{vc} = 2.6;	Av_{mc} = 6.6;	t = 24.68;	***

TABLE 20. - Statistical comparison of averages by pyrite - Con.

Robena/Maple Creek ($n_r + n_{mc} - 2 = 23$)					
Iron II:	Av_r = 0.002;	Av_{mc} = 3.4;	t = 2.81;	**
Iron Total:	Av_r = 0.044;	Av_{mc} = 3.9;	t = 3.15;	**
Sulfate:	Av_r = 310;	Av_{mc} = 348;	t = 0.62;	NS
Acidity:	Av_r = -8;	Av_{mc} = 5;	t = 2.21;	*
pH:	Av_r = 7.1;	Av_{mc} = 6.6;	t = 1.35;	NS
Inhibitor - Fly Ash				
Valley Camp/Maple Creek ($n_{vc} + n_{mc} - 2 = 30$)				
Iron II:	Av_{vc} = 0.16;	Av_{mc} = 0.006;	t = 6.48;	***
Iron Total:	Av_{vc} = 4.1;	Av_{mc} = 0.067;	t = 6.24;	***
Sulfate:	Av_{vc} = 425;	Av_{mc} = 652;	t = 1.65;	NS
Acidity:	Av_{vc} = 88;	Av_{mc} = -17;	t = 7.91;	***
pH:	Av_{vc} = 3.2;	Av_{mc} = 7.4;	t = 15.52;	***
Inhibitor - Slag				
Valley Camp/Maple Creek ($n_{vc} + n_{mc} - 2 = 41$)				
Iron II:	Av_{vc} = 0.008;	Av_{mc} = 0.18;	t = 1.23;	NS
Iron Total:	Av_{vc} = 0.20;	Av_{mc} = 0.87;	t = 2.62;	*
Sulfate:	Av_{vc} = 348;	Av_{mc} = 351;	t = 0.07;	NS
Acidity:	Av_{vc} = -16;	Av_{mc} = -14;	t = 0.68;	NS
pH:	Av_{vc} = 7.0;	Av_{mc} = 6.3;	t = 3.30;	**

Subscript vc = Valley Camp
Subscript r = Robena
Subscript mc = Maple Creek
t = "Student" t

*** Significant at 99.9% confidence level
** Significant at 99% confidence level
* Significant at 95% confidence level
NS Not Significant at 95% Confidence Level

STOICHIOMETRY OF INHIBITED PYRITE SYSTEMS

The average values of the several reaction products obtained during the experimental study have also been interpreted in terms of chemical stoichiometry to estimate how much pyrite is actually oxidized and to determine the quantity of the insoluble oxidation products. The interpretation consists of a materials balance around the equations:

$$FeS_2 + 7/2\ O_2 + H_2O \longrightarrow FeSO_4 + H_2SO_4$$

$$FeSO_4 + 1/4\ O_2 + 1/2\ H_2SO_4 \longrightarrow 1/2\ Fe_2(SO_4)_3 + 1/2\ H_2O$$

$$1/2\ Fe_2(SO_4)_3 + 3\ H_2O \longrightarrow Fe(OH)_3 + 3/2\ H_2SO_4$$

$$H_2SO_4 + MO(MCO_3) \longrightarrow MSO_4 + H_2O + (CO_2)$$

where M is a divalent alkaline earth cation, e.g., Ca^{++} or Mg^{++}, or two monovalent alkali metal cations, e.g., $2\ Na^{+}$.

The following assumptions were made concerning the oxidation of pyrite.

* The only source of sulfate ($SO_4^{=}$) is from the oxidation of pyrite (FeS_2). Therefore, the number of moles of pyrite which has been oxidized is half the number of moles of sulfate determined.

* The iron content of the pyrite can be found as ferrous ion (Fe^{++}), and ferric ion (Fe^{+++}) in solution, and as insoluble ferric hydroxide ($Fe(OH)_3$). The amount of insoluble $Fe(OH)_3$ can be estimated from the difference of total iron in solution (from the total iron analyses) and the quantity of iron in pyrite (from the sulfate analyses as described above).

* The acidity measurements reflect both acid generated and iron in solution. When aqueous samples are titrated with standard base, hydroxide ion will be consumed to precipitate both ferrous and ferric ions as well as to neutralize free acid. Therefore, free acid (H^{+}) is estimated by taking the difference between equivalents of acid consumed in the analyses and the equivalents of both ferrous and ferric ion in solution.

* Acid can also be consumed by neutralizing alkaline materials naturally present in the pyrites or by alkalinity in the inhibitors. These neutralizing reactions will result in soluble cations in the solution. Furthermore, any alkalinity present in solution is assumed to be due to bicarbonate (HCO_3^-). Thus, the negative acidities determined by acidity and alkalinity measurements during the program have been assumed to be bicarbonate product from pyrite oxidation and subsequent neutralization by alkaline components of the system.

* The quantity of soluble cation species arising from the neutralization can be estimated from an anion/cation balance of the aqueous system. The equivalents of anion are determined by sulfate measurements and bicarbonate estimates; the equivalents of cation are determined from ferrous ion, ferric iron, and free acid values. The difference between equivalents of anion and equivalents of cation to establish electrical balances thus becomes the number of equivalents of alkaline earth cation (M^{++}) present in the system.

* Oxygen (O_2) consumed in the reaction can be estimated by multiplying the moles of pyrite by 3.5 to generate sulfite; and multiplying the moles of pyritic iron less moles of ferrous ion by 0.25 to generate ferric ion in solution and iron as insoluble ferric hydroxide. The sum of the two values then is the number of moles of oxygen consumed in the pyrite oxidation.

Estimates of the quantities of reactants and products using these preceding assumptions are presented in Table 21. The units of entries in the table are millimoles of particular species generated per kilogram of pyrite per week of exposure to flowing moist air.

As can be seen from entries in this table, the Valley Camp No. 1 control experiment resulted in the highest consumption of pyrite with generation of the most reaction products. Most of the iron from the pyrite oxidation went to form soluble ferric ion, and very little reacted to form insoluble ferric hydroxide. Results from the Robena and Maple Creek control experiments indicate less pyrite consumed. However, the iron reaction products in these two cases are estimated to be primarily as insoluble ferric hydroxide rather than as soluble ferric or ferrous ion. These results suggest that if there is sufficient in situ neutralizing capacity available in the pyrites, large quantities of acid mine drainage will not be generated.

TABLE 21. - Stoichiometries of pyrite oxidation as determined from experimental results (m mole/kg/week)

System	Reactants		$\xrightarrow{H_2O}$	Products						
	FeS_2	O_2	$\xrightarrow{MO, MCO_3}$	SO_4^{--}	H^+	Fe^{++}	Fe^{+++}	HCO_3^-	M^{++}	$Fe(OH)_3$
Valley Camp - Control	5.98	22.28	→	11.95	3.76	0.48	5.00	0	2.09	0.50
Valley Camp - Nails	4.15 FeS_2 0.03 Fe	15.41	→	8.30	1.20	0.64	3.54	0	1.75	0
Valley Camp - Fly Ash	2.21	8.30	→	4.43	1.54	0.003	0.07	0	3.55	2.41
Valley Camp - Slag	1.81	6.79	→	3.62	0	0.0001	0.0002	0.32	3.78	1.81
Valley Camp - Portland Cement	0.23	0.86	→	0.46	0	0.0005	0.01	2.30	1.59	0.22
Valley Camp - Kiln Dust	1.71	6.41	→	3.42	0	0.0005	0.004	4.74	5.78	1.70
Robena - Control	1.61	6.03	→	3.22	0	0.0002	0.005	0.32	3.37	1.60
Robena - Nails	1.61	6.05	→	3.23	0	0.0001	0.002	0.16	3.31	1.61
Maple Creek - Control	1.65	6.17	→	3.29	0	0.0003	0.008	0.46	3.51	1.64
Maple Creek - Nails	1.62	6.78	→	3.63	0	0.06	0.009	0.05	3.58	1.55
Maple Creek - Fly Ash	3.40	12.71	→	6.79	0	0.0001	0.001	0.34	6.96	3.40
Maple Creek - Slag	1.83	6.86	→	3.66	0	0.003	0.012	0.28	3.78	1.82

Lesser quantities of reaction products are generated in the Valley Camp iron nail-inhibited system than those of the control system. All of the iron can be accounted for in the soluble forms (ferrous and ferric), and some iron from the nails must be included to make the iron materials balance. However, the Fe^{+++}/Fe^{++} ratio in the nail-inhibited system is 5.53 whereas the same ratio in the central system is 10.42. Smith et al. (3) have determined pyrites oxidation as a function of Fe^{+++}/Fe^{++} ratios and have shown that the greater the ferric/ferrous ratio, the greater is the pyrite oxidation rate. The data obtained from the Valley Camp No. 1 nail-inhibited experiments support this observation. In the practical sense, the decrease in rate of oxidation in the nail-inhibited system is only about 20%. However, free acid in the inhibited system is about one-third of that of the control system which is a substantial decrease of this component. The lesser amount of acid generated is offset somewhat by a proportional increase in the amount of soluble iron species. Nevertheless, the data suggest that, if one can keep the soluble iron in the ferrous state, the rate of generation of acid mine drainage can be reduced.

In the iron nail-inhibited Robena and Maple Creek systems, little or no inhibition is noted. Since these systems did not generate acid in the control experiments, the lack of effect by the iron nails is not unexpected.

In the remaining Valley Camp No. 1 systems inhibited with fly ash, slag, portland cement, and kiln dust, the amount of pyrite oxidized is substantially less than the amount of pyrite oxidized in the control experiment (and in the iron nail-inhibited experiment). Indeed the quantities of pyrite oxidized are about the same as those observed in the nonacid-producing Robena and Maple Creek systems. The common thread throughout all of these systems is the presence of ferric hydroxide as the end product of pyritic irons. In addition, soluble iron is virtually absent reaction product. In the small quantities of soluble iron, the Fe^{+++}/Fe^{++} ratios are high, which would be expected because of pH conditions on the alkaline side. However, since absolute concentrations of iron ionic species are so very small, their effect on pyrite oxidation rates is also small.

Thus, we conclude that, if the iron products generated from pyrite oxidation can be made insoluble <u>at the source</u> of generation, it is possible to inhibit acid mine drainage formation by chemical means. Suggested mechanisms for the inhibition are discussed next.

MECHANISM OF INHIBITING ACID MINE DRAINAGE FORMATION

Results of the experimental program strongly support the concept that soluble ferric iron (iron III) is a key oxidant for acid mine drainage formation.

$$14\ Fe^{+++} + FeS_2 + 8\ H_2O \longrightarrow 15\ Fe^{++} + 2\ SO_4^{=} + 16\ H^{+}$$

If soluble ferric iron can be eliminated from the system, then acid (H^{+}) cannot be formed by the above reaction. It would have to be formed by direct oxidation of pyrite with oxygen in a slow reaction.

$$FeS_2 + 7/2\ O_2 + H_2O \longrightarrow Fe^{++} + 2\ SO_4^{=} + 2\ H^{+}$$

The various inhibitors evaluated in the study operate by two mechanisms--minimization of soluble ferric ion and insolubilization of ferric ion. The iron nail-inhibited systems operate in the mode of minimizing soluble ferric ion. The metallic iron is a stronger reducing agent than pyrite. Thus, ferric ion which is formed by oxidation of ferrous iron (either directly with air or biochemically with ferro-oxidans) will be reduced back to ferrous iron.

$$Fe^{+++} + Fe \longrightarrow 2\ Fe^{++}$$

On the other hand, ferric iron can be immobilized in systems involving fly ash or blast furnace slag. When the acid-producing Valley Camp No. 1 pyrite was treated with these materials, very little soluble iron was formed. The analytical data indicate that the alkalinity was sufficient to precipitate iron and neutralize any acid which was formed. However, less pyrite was oxidized when in the presence of the fly ash or blast furnace slag indicating an inhibitory effect on acid mine drainage formation. Thus, we view these materials as sinks for ferrous iron which would keep the iron in an insoluble form. Once ferrous iron (or other iron reaction products) are immobilized in the inhibitor matrix, their oxidation to soluble ferric iron and subsequent formation of acid mine drainage is slowed substantially.

The more alkaline inhibitors evaluated, portland cement and kiln dust, are believed to operate in a similar mechanism. Since these materials do contain substantial quantities of hydroxide, insolubilization of ferrous iron by precipitation as ferrous hydroxide and subsequent oxidation to ferric hydroxide cannot be ruled out.

$$Fe^{++} + 2\ OH^{-} \longrightarrow Fe(OH)_2$$

$$Fe(OH)_2 + 1/2\ H_2O + 1/4\ O_2 \longrightarrow Fe(OH)_3$$

As far as mechanism is concerned, it makes no difference whether iron reaction products are in the ferrous or ferric state. The important factor is that the iron reaction products be insoluble.

The decreased levels of sulfate observed with time in the experiments with alkaline inhibitors (fly ash, slag, cement, and kiln dust) from comparable levels observed in the control experiments can be explained in one of three ways. First, these materials may have coated the pyrite to exclude air for the oxidation. However, we do not believe that coating would be sufficient to prevent pyrite contact with oxygen. Rather, it appears that the coating may provide means of regulating surficial pH and iron reaction product solubility which regulates pyrite oxidation. Second, sulfate can become immobilized along with iron in the silicate matrix of the inhibitors. This mechanism cannot be ruled out based on the experimental evidence. Reaction products such as basic ferric sulfate ($FeOHSO_4$) could very well be present and not washed away during column flushing with water. Third, the materials acted as inhibitors for sulfur and iron bacteria in the system. This mechanism is quite possible. Bacterial colonies were found in the Valley Camp No. 1 pyrite but not in the Robena or Maple Creek pyrites. Nor could Robena or Maple Creek pyrite be made to produce acid even when inoculated with bacteria. Thus, it appears that bacterial oxidation of pyrite may be important in some pyrites but not others. Finally, the rates of pyrite oxidation in Robena and Maple Creek may be slower than that of Valley Camp No. 1. The as-received Robena and Maple Creek were fairly acid, but the acidity was washed away when used in the experiments. It might be that the weekly cycle of washing was too short a time for these pyrites to generate many oxidation products.

Whatever the actual mechanism might be, our findings are consistent with those of other observers. Singer and Stumm (4) postulate that acid mine drainage formation is initiated by direct oxidation of pyrite with oxygen and propagated by reaction of ferric iron with pyrite.

Initiator reaction:

$$FeS_2(s) \xrightarrow{(+ O_2)} Fe^{++} + \text{S-compound}$$

Propagation cycle:

$$Fe^{++} + O_2 \xrightarrow{\text{slow}} Fe^{+++}$$

$$Fe^{+++} + FeS_2(s) \xrightarrow{\text{fast}} Fe^{++} + SO_4^{=}$$

The rate determining step in the process is oxidation of ferrous iron in solution. The rate of soluble ferrous iron oxidation to soluble ferric ion is accelerated by microorganisms in the system. Whether ferrous oxidation is chemical or biological, control of the ferrous-ferric reaction couple is necessary to control formation of acid in mine drainage formation.

A second mechanism postulated for acid mine drainage formation has been developed by Smith et al. (3). The mechanism proposed by these authors is strictly chemical and involves four steps.

1. Ferric ion is adsorbed in a "reactive site" of pyrite to form an activated complex.

2. Ferrous ion is adsorbed on the reactive site.

3. The activated complex decomposes to yield an adsorbed ferrous ion and transfer of electrons.

4. Desorption of adsorbed ferrous ion occurs.

The authors suggest that Step No. 3, the surface transfer of electrons, is the rate-controlling step in oxidation of pyrite. It is our opinion that the transfer of electrons in Step No. 3 involves the movement of electrons from the sulfide in pyrite to the adsorbed ferric ion of Step No. 1. Since it takes 14 ferric ions to produce two sulfate ions from 1 mole of pyrite, the mechanism proposed would involve the adsorption

of many ferric ions in Step No. 1 of the process to complete the oxidation of pyrite to sulfuric acid and ferrous sulfate.

Although the two theories of mine drainage formation disagree on what is the rate-controlling step, they do agree that reaction of pyrite with ferric ion in solution is a key step in forming mine drainage. In the case of acid mine drainage inhibition, one needs to minimize the quantity of soluble ferric iron to prevent the occurrence of Step No. 1. If there is no ferric iron to be absorbed from solution for Step No. 1, then the rate-controlling electron transfer at Step No. 3 cannot occur and no acid mine drainage will be formed.

The mechanisms developed by Singer and Stumm (4) and by Smith et al. (3) both require the availability of ferric ion in solution for rapid formation of acid mine drainage. From our evaluation of experimental data generated during this program, we have also concluded that aqueous ferric ion is a key constituent in acid mine drainage formation. Our observations have been that if iron products from pyrite oxidation are insoluble then lesser quantities of pyrite are oxidized as reflected by sulfate concentration in reacted pyrite leachate. We have therefore concluded that, if conditions can be maintained such that iron oxidation products are kept insoluble, formation of acid mine drainage can be inhibited by chemical methods.

Other researchers have observed that coating pyrite with alkaline silicates (5, 6) will reduce formation of acid mine drainage. However, results have been interpreted as being due to exclusion of oxygen from the pyritic surface rather than true chemical inhibition. When the results of silicate coating inhibition experiments are reevaluated in terms of the mine drainage formation mechanism, the data suggest that such coatings can be considered as real chemical inhibitors rather than as coatings to exclude air. The alkali silicate coatings will provide sites to which ferric ion can preferentially absorb rather than on pyritic surfaces. In addition, the pH conditions created by the alkali silicate coatings may be sufficiently high to deter the proliferation of iron-oxidizing bacteria by reducing the amount of soluble iron available for food. Thus, the alkali silicates may function as immobilizers of both ferrous and ferric ions which prevent acid mine drainage formation rather than as coatings to exclude air. When reinterpreted from this point of view, the results showing decreased formation of mine drainage after the coating materials should have been washed away become explainable.

It is our feeling, based upon our results and those of other researchers, that removal of soluble ferric iron from the system is a viable means of preventing acid mine drainage formation. Our results have clearly shown that if a reducing agent stronger than pyrite, i.e., iron nails, is in contact with pyrite, mine drainage products, e.g., sulfate and acidity, can be reduced. Metallic iron will keep ferric ion concentrations low. However, it will also produce ferrous ion in the process, and hence is not completely satisfactory as an inhibition agent. On the other hand, if soluble ferric iron can be immobilized by sorption on a substrate other than pyrite, then this mechanism too becomes a means of inhibiting mine drainage formation. It is this latter mechanism which we believe to be the more viable approach.

CONCLUSIONS

Conclusions drawn from the experimental study follow:

1. Chemical inhibition of acid mine drainage formation can be achieved with alkaline siliceous materials. Blast furnace slag and portland cement are quite attractive inhibitors.

2. Bacteria are important in determining the amount of acid mine drainage from pyrite oxidation. Their primary role is to oxidize ferrous ion to ferric ion, the latter as being an important oxidizer of pyrite.

3. Oxidation of pyrite with ferric ion is the key reaction in acid mine drainage formation. If ferric ion can be minimized or if it can be immobilized, quantities of pyrite oxidation products found in mine drainage are greatly reduced.

4. Coating pyrite with inorganic materials inhibit mine drainage by insolubilizing ferric (and perhaps ferrous) ion to remove them from the aqueous reaction medium. Since the iron species are in an insoluble form, rapid oxidation of ferrous hydroxide to ferric hydroxide under the neutral or alkaline conditions of the system has little effect on generation of acid mine drainage.

5. The measurement of pH is not a definitive indicator of the amount of acid mine drainage produced. When fly ash was used as an inhibitor, pHs approaching that of the noninhibited system were observed; however, the quantities of pyrite oxidation products in the drainage, e.g., sulfate and acidity were small compared to those of the control sample.

RECOMMENDATIONS

Recommendations drawn from the experimental work are:

1. Determine lifetime of alkaline siliceous inhibitors. Experiments with fly ash and slag were conducted up to 25 weeks at the end of which acid mine drainage formation was still being inhibited. How long the inhibition would last needs to be established more precisely.

2. Optimize dosage of alkaline siliceous inhibitors. Inhibitors were used at a ratio of 1 part inhibitor to 5 parts pyrite in the experimental study. This ratio is much higher than necessary or desirable for widespread application. Additional work is needed to determine just how much inhibitor is adequate.

3. Develop methods for applying inhibitor. On the basis of the studies conducted, we believe that one might apply a portland cement or blast furnace slag inhibitor by a modified gunite process, i.e., blowing inhibitor onto exposed pyrite surfaces in a coal mine. Additional results for the lifetime and dosage studies described above are needed to establish whether this approach is viable or whether other approaches for application are more practical.

4. Additional pyrite types should be tested representing a wide variety of tendencies to form acid mine drainage. Variability should include crystalline form of pyrite, and composition of shale matrix in which pyrite is found.

5. Economic assessment of each technically feasible inhibitor should be undertaken. This assessment would include logistics of transporting inhibitor to the site, quantity of inhibitor required, preparation costs for applying inhibitor, and availability of inhibitor for specific regions of the country.

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APPENDIX A

EXPERIMENTAL DATA FROM SCREENING EXPERIMENTS

Pyrite	Reaction time (days)	Pyrite (g)	Inhibitor (g)	pH	Iron II (mg/g)	Total Iron (mg/g)	Sulfate (mg/g)	Acidity (mg $CaCO_3$/g)	Alkalinity (mg $CaCO_3$/g)
Reference: Dried pyrite washed with 200 ml H_2O									
Robena	0.5 hr	5	0	6.3	-	< 0.01	1.40	0.11	0.77
Maple Creek	0.5 hr	5	0	6.7	-	< 0.1	0.99	0.11	0.93
Valley Camp No. 1	0.5 hr	5	0	4.8	-	0.06	4.24	0.82	0.13
Valley Camp No. 3	0.5 hr	5	0	6.6	-	< 0.01	2.36	0.13	0.69
Kraft Coarse	0.5 hr	5	0	5.2	-	0.06	1.48	0.94	0.28
Kraft Intermediate	0.5 hr	5	0	2.9	-	0.60	23.55	22.67	0
Experiment No. 1: Dried pyrite in tubes, moist air passed through, leached with 200 ml H_2O									
Robena	7	25	0	6.4	-	< 0.01	2.04	0.10	0.12
Maple Creek	7	25	0	6.4	-	< 0.01	1.67	0.05	0.22
Valley Camp No. 1	7	25	0	5.9	-	0.04	5.32	0.19	0.02
Valley Camp No. 3	7	25	0	5.1	-	< 0.01	3.07	0.08	0.20
Kraft Coarse	7	25	0	4.4	-	0.20	1.73	1.04	0.01
Kraft Intermediate	7	25	0	2.1	-	0.98	26.00	12.67	0
Experiment No. 2: Wet washed pyrite in tubes, moist air passed through, leached with 200 ml H_2O									
Robena	6	25	0	6.4	-	< 0.01	1.40	0.05	0.27
Maple Creek	6	25	0	7.5	-	< 0.01	0.86	0.06	0.32
Valley Camp No. 1	6	25	0	6.2	-	< 0.01	1.58	0.04	0.15
Valley Camp No. 3	6	25	0	6.5	-	< 0.01	0.41	0.06	0.29
Kraft Coarse	6	25	0	4.2	-	0.04	0.16	0.14	0
Kraft Intermediate	4	25	0	1.3	-	0.09	0.45	0.23	0
Experiment No. 3: Wet washed pyrite in tubes, dry air passed through, leached with 200 ml H_2O									
Robena	6	25	0	6.9	-	< 0.01	1.40	0.03	0.25
Maple Creek	6	25	0	7.6	-	< 0.01	0.46	0.04	0.24
Valley Camp No. 1	6	25	0	6.3	-	< 0.01	0.67	0.03	0.12
Valley Camp No. 3	6	25	0	6.8	-	< 0.01	0.26	0.04	0.24
Kraft Coarse	6	25	0	4.4	-	0.01	0.03	0.07	0.01
Kraft Intermediate	6	25	0	1.0	-	0.01	0.72	0.58	0
Experiment No. 4: Dried pyrite, leached with 50 ml distilled H_2O daily, dry air passed over pyrite, leachate accumulated for analysis									
Maple Creek	5	17	0	6.8	-	< 0.01	1.50	0.10	0.41
Robena	5	14	0	6.2	-	< 0.01	1.67	0.08	0.12
Valley Camp No. 1	5	14	0	5.0	-	0.02	5.83	0.89	0.06
Valley Camp No. 3	5	10	0	6.8	-	< 0.01	1.42	0.14	0.86
Kraft Coarse	5	17	0	1.1	-	0.04	1.56	1.19	0

Pyrite	Reaction time (days)	Pyrite (g)	Inhibitor (g)	pH	Iron II (mg/g)	Total iron (mg/g)	Sulfate (mg/g)	Acidity (mg $CaCO_3$/g)	Alkalinity (mg $CaCO_3$/g)
Experiment No. 5: Wet pyrite from Experiment No. 4, leached with 50 ml distilled H_2O daily, moist air passed through pyrite, leachate accumulated for analysis									
Maple Creek	5	17	0	6.0	-	< 0.01	0.70	0.08	0.25
Robena	5	14	0	5.2	-	< 0.01	1.07	0.15	0.02
Valley Camp No. 1	5	14	0	3.7	-	< 0.01	1.56	0.25	0
Valley Camp No. 3	5	10	0	6.6	-	< 0.01	0.37	0.10	0.85
Kraft Coarse	5	37	0	3.5	-	0.03	0.16	0.17	0
Experiment No. 6: Wet pyrite from Experiment Nos. 4 and 5, leached with 50 ml distilled H_2O daily, dry air passed through wet pyrite, leachate accumulated for analysis									
Maple Creek	7	17	0	6.6	-	< 0.01	0.29	0.09	0.39
Robena	7	14	0	6.4	-	< 0.01	0.37	0.11	0.23
Valley Camp No. 1	7	14	0	4.8	-	< 0.01	1.03	0.14	0.05
Valley Camp No. 3	7	10	0	6.5	-	< 0.01	0.12	0.08	0.63
Kraft Coarse	7	37	0	3.5	-	0.01	0.20	0.21	0
Experiment No. 7: Wet pyrite from Experiment Nos. 4 through 6, spread on watch glass and dried for 2 weeks, washed with distilled water									
Maple Creek	13	17	0	6.1	-	< 0.01	0.14	0.02	0.19
Robena	13	14	0	6.4	-	< 0.01	0.20	0.06	0.17
Valley Camp No. 1	13	14	0	6.2	-	< 0.01	0.31	0.06	0.14
Valley Camp No. 3	13	10	0	6.4	-	< 0.01	0.06	0.08	0.32
Kraft Coarse	13	37	0	6.4	-	< 0.01	0.05	0.03	0.03
Experiment No. 8: Fresh sample of dried pyrite, washed with 200 ml of distilled water, wash water analyzed									
Maple Creek	30 min	17	0	6.4	-	< 0.01	1.09	0.09	0.24
Robena	30 min	14	0	6.0	-	0.01	1.19	0.11	0.17
Valley Camp No. 1	30 min	14	0	5.7	-	0.03	3.57	0.51	0.09
Valley Camp No. 3	30 min	10	0	6.3	-	< 0.01	2.00	0.12	0.52
Kraft Coarse	30 min	37	0	4.2	-	0.04	1.80	1.41	0
Experiment No. 9: Fresh sample of dried pyrite, washed with 200 ml "electrolyte" (100 mg $CaCl_2$/ℓ, 100 mg $NaNO_3$/ℓ); wash water analyzed									
Maple Creek	30 min	17	0	5.6	-	0.01	0.87	0.05	0.12
Robena	30 min	14	0	5.5	-	0.03	1.03	0.17	0.11
Valley Camp No. 1	30 min	14	0	3.7	-	0.09	2.69	0.86	0
Valley Camp No. 3	30 min	10	0	6.4	-	< 0.01	1.95	0.16	0.58
Kraft Coarse	30 min	37	0	3.6	-	0.09	1.46	1.41	0

Pyrite	Reaction time (days)	Pyrite (g)	Inhibitor (g)	pH	Iron II (mg/g)	Total iron (mg/g)	Sulfate (mg/g)	Acidity (mg $CaCO_3$/g)	Alkalinity (mg $CaCO_3$/g)
Experiment No. 10: Valley Camp No. 1 pyrite, washed with electrolyte (100 mg $CaCl_2/\ell$, 100 mg $NaNO_3/\ell$), washed pyrite in contact with ground limestone, moist air passed through pyrite, leached with 50 ml electrolyte daily, composite leachate analyzed									
Control - no limestone	7	14	0	3.8	0.004	0.009	1.65	0.24	0
Limestone below pyrite	7	14	3.5	6.8	< 0.001	0.001	2.51	0.24	0.86
Limestone above pyrite	7	14	3.5	6.7	< 0.001	0.019	2.13	0.14	0.37
Limestone mixed with pyrite	7	14	3.5	6.5	< 0.001	< 0.001	2.10	0.28	0.81
Experiment No. 10a: Continuation of Experiment No. 10, moist air passed through pyrite for 6 days, washed with 200 ml of electrolyte									
Control - no limestone	6	14	0	5.1	0.005	0.008	1.07	0.08	0.01
Limestone below pyrite	8	14	3.5	7.9	< 0.001	< 0.001	1.11	0.10	0.61
Limestone above pyrite	8	14	3.5	7.7	< 0.001	< 0.001	0.36	0.09	0.51
Limestone mixed with pyrite	6	14	3.5	7.9	< 0.001	< 0.001	1.45	0.10	0.64
Experiment No. 11: Valley Camp No. 1 pyrite, washed with electrolyte (100 mg $CaCl_2/\ell$, 100 mg $NaNO_3/\ell$), washed pyrite in contact with iron filings, moist air passed through pyrite, leached daily with 50 ml electrolyte, composited leachate analyzed									
Control - no iron filings	5	14.0	0	3.7	0.002	0.004	1.26	0.22	0
Iron filings below pyrite	5	14.0	9.5	5.0	0.015	0.020	0.87	0.24	0.05
Iron filings above pyrite	5	14.0	9.5	6.7	< 0.001	0.001	0.81	0.18	0.26
Iron filings mixed with pyrite	5	14.0	9.5	5.1	0.008	0.014	0.34	0.14	0.06
Iron filings - no pyrite	5	0	46.4	6.8	< 0.001	< 0.001	0.09	0.05	0.01
Experiment No. 11a: Continuation of Experiment No. 11, samples leached with 200 ml of electrolyte after 8 days, collected leachate analyzed									
Control - no iron filings	8	14.0	0	5.8	0.002	0.004	1.18	0.08	0.11
Iron filings below pyrite	8	14.0	9.5	5.6	0.018	0.021	1.01	0.22	0.05
Iron filings above pyrite	8	14.0	9.5	7.2	< 0.001	0.001	0.28	0.11	0.26
Iron filings mixed with pyrite	8	14.0	9.5	6.2	0.011	0.017	0.13	0.15	0.09
Iron filings - no pyrite	8	0	46.4	9.4	< 0.001	< 0.001	0.03	0	0.11
Experiment No. 11b: Continuation of Experiment Nos. 11 and 11a, samples leached with 200 ml of electrolyte after 3 days, collected leachate analyzed									
Control - no iron filings	3	14.0	0	5.1	0.003	0.005	0.53	0.08	0.05
Iron filings below pyrite	3	14.0	9.5	6.0	0.004	0.015	0.54	0.12	0.06
Iron filings above pyrite	3	14.0	9.5	7.1	< 0.001	0.001	0.12	0.08	0.11
Iron filings mixed with pyrite	3	14.0	9.5	6.6	< 0.001	0.007	0.07	0.08	0.08
Iron filings - no pyrite	3	0	46.4	9.6	Nil	< 0.001	0.05	0	0.12
Experiment No. 12: Rohens pyrite, washed with electrolyte, washed pyrite in contact with iron filings, moist air passed through pyrite, leached daily with 50 ml electrolyte, composited leachate analyzed									
Control - no iron filings	6	14.0	0	4.6	0.001	0.002	1.19	0.19	0
Iron filings below pyrite	6	14.0	9.5	6.5	Nil	0.004	1.11	0.14	0.08
Iron filings above pyrite	6	14.0	9.5	5.0	0.001	0.002	1.45	0.16	0.05
Iron filings mixed with pyrite	6	14.0	9.5	6.0	Nil	0.001	0.15	0.08	0.11
Iron filings - no pyrite	6	0	46.4	7.1	Nil	< 0.001	0.09	0.02	0.04

Pyrite	Reaction time (days)	Pyrite (g)	Inhibitor (g)	pH	Iron II (mg/g)	Total iron (mg/g)	Sulfate (mg/g)	Acidity (mg $CaCO_3$/g)	Alkalinity (mg $CaCO_3$/g)
Experiment No. 12a: Continuation of Experiment No. 12, samples leached with 200 ml of electrolyte after 7 days, collected leachate analyzed									
Control - no iron fillings	7	14.0	0	6.7	< 0.001	0.001	1.26	0.05	0.16
Iron fillings below pyrite	7	14.0	9.5	7.4	< 0.001	0.010	1.14	0.09	0.19
Iron fillings above pyrite	7	14.0	9.5	7.3	Nil	0.002	1.38	0.09	0.11
Iron fillings mixed with pyrite	7	14.0	9.5	6.9	< 0.001	0.014	0.04	0.08	0.13
Iron fillings - no pyrite	7	0	46.4	8.6	Nil	0.002	0.02	0.01	0.05
Experiment No. 13: Valley Camp No. 1 pyrite, samples used in Experiment Nos. 12, 12a, and 12b covered with 1/2-in. layer of -10 to +200 mesh marble chips, leached daily with 50 ml electrolyte, composited leachate analyzed									
Control - no iron fillings or marble chips	6	14.0	0	4.9	0.008	0.012	1.04	0.17	0.06
Iron fillings below pyrite, marble chips above pyrite	6	14.0	9.5	6.4	< 0.001	0.018	0.99	0.14	0.14
Iron fillings above pyrite, marble chips above iron fillings	6	14.0	9.5	6.7	< 0.001	0.003	0.18	0.14	0.22
Iron fillings mixed with pyrite, marble chips above mixture	6	14.0	9.5	6.8	< 0.001	0.007	0.12	0.15	0.21
Iron fillings - no pyrite, marble chips above iron fillings	6	14.0	46.4	9.3	Nil	< 0.001	0.05	0	0.16
Experiment No. 14: Robena pyrite, samples used in Experiment Nos. 12 and 12 covered with 1/2-in. layer of -10 to +200 mesh marble chips, leached daily with 50 ml of electrolyte, composited leachate analyzed									
Control - no iron fillings or marble chips	7	14.0	0	6.5	< 0.001	0.001	1.59	0.05	0.18
Iron fillings below pyrite, marble chips above pyrite	7	14.0	9.5	7.2	< 0.001	0.005	1.33	0.13	0.27
Iron fillings above pyrite, marble chips above pyrite	7	14.0	9.5	7.4	< 0.001	0.002	1.54	0.13	0.43
Iron fillings mixed with pyrite, marble chips above mixture	7	14.0	9.5	7.3	Nil	0.003	0.04	0.10	0.23
Iron fillings - no pyrite, marble chips above iron fillings	7	0	46.4	7.6	Nil	0.006	0.03	0.06	0.05
Experiment No. 15: All pyrite samples washed with electrolyte, iron fillings (1/2-in. thick) sandwiched between pyrite in column, moist air passed through pyrite, leached daily with 50 ml of electrolyte, composited leachate analyzed									
Valley Camp No. 1 - iron filing sandwich	6	11.0	9.5	5.2	0.025	0.030	2.04	0.20	0.07
Robena - iron filing sandwich	6	11.0	9.5	6.8	< 0.001	0.003	1.96	0.16	0.20
Maple Creek - iron filing sandwich	6	13.4	9.5	7.8	< 0.001	0.003	0.53	0.14	0.28
Valley Camp No. 3 - iron filing sandwich	6	7.8	9.5	8.1	< 0.001	0.002	0.48	0.29	0.68
Kraft Coarse - iron filing sandwich	6	29.2	9.5	4.9	0.011	0.013	0.52	0.40	0.01

Pyrite	Reaction time (days)	Pyrite (g)	Inhibitor (g)	pH	Iron II (mg/g)	Total iron (mg/g)	Sulfate (mg/g)	Acidity (mg $CaCO_3$/g)	Alkalinity (mg $CaCO_3$/g)
Experiment No. 16: Same conditions as Experiment No. 15, except that a mixture of iron filing and marble chips (1:1 by weight) was used as the 1/2-in. sandwich									
Valley Camp No. 1 - iron filing/marble chip sandwich	6	11.0	6.4	6.6	< 0.001	0.006	1.64	0.16	0.16
Robena - iron filing/marble chip sandwich	6	11.0	6.4	6.6	< 0.001	0.002	1.82	0.17	0.17
Maple Creek - iron filing/marble chip sandwich	6	11.4	6.4	6.9	< 0.001	0.004	0.56	0.14	0.24
Valley Camp No. 3 - iron filing/marble chip sandwich	6	7.8	6.4	6.9	0.003	0.011	1.66	0.23	0.14
Kraft Coarse - iron filing/marble chip sandwich	6	29.2	6.4	4.9	0.011	0.011	0.49	0.53	0.02
Experiment No. 17: All pyrite samples washed with electrolyte, washed pyrite mixed with iron filings and marble chips, iron filings/marble chip mixture 1:1 by weight, leached daily with 50 ml electrolyte, composite leachate analyzed									
Valley Camp No. 1 - mixture of pyrite with 3:1 iron filings/marble chips	6	11.0	5.0	6.2	0.003	0.010	1.44	0.17	0.14
Robena - mixture of pyrite with 3:1 iron filings/marble chips	6	11.0	5.0	7.2	< 0.001	0.001	0.41	0.10	0.30
Maple Creek - mixture of pyrite with 3:1 iron filings/marble chips	6	11.4	5.0	8.1	< 0.001	0.004	0.29	0.05	0.44
Valley Camp No. 3 - mixture of pyrite with 3:1 iron filings/marble chips	6	7.8	5.0	7.3	Nil	0.001	0.53	0.14	0.51
Kraft Coarse - mixture of pyrite with 3:1 iron filings/marble chips	6	29.2	5.0	6.7	0.008	0.011	0.42	0.10	0.04
Experiment No. 17a: Continuation of Experiment No. 17									
Valley Camp No. 1 - mixture of pyrite with 3:1 iron filings/marble chips	6	11.0	5.0	6.2	< 0.001	< 0.001	0.58	0.14	0.66
Robena - mixture of pyrite with 3:1 iron filings/marble chips	6	11.0	5.0	6.4	< 0.001	0.001	0.26	0.17	0.40
Maple Creek - mixture of pyrite with 3:1 iron filings/marble chips	6	11.4	5.0	6.1	< 0.001	0.001	0.21	0.45	0.71
Valley Camp No. 3 - mixture of pyrite with 3:1 iron filings/marble chips	6	7.8	5.0	6.4	< 0.001	0.002	0.12	0.34	0.48
Kraft Coarse - mixture of pyrite with 3:1 iron filings/marble chips	6	29.2	5.0	6.0	< 0.001	< 0.001	0.12	0.12	0.12

Pyrite	Reaction time (days)	Pyrite (g)	Inhibitor (g)	pH	Iron II (mg/g)	Total iron (mg/g)	Sulfate (mg/g)	Acidity (mg $CaCO_3$/g)	Alkalinity (mg $CaCO_3$/g)	Aluminum (mg/g)
Experiment No. 18: All pyrite samples washed with electrolyte, washed pyrite mixed with aluminum chips, leached daily with 50 ml electrolyte, composite leachate analyzed										
Valley Camp No. 1 - mixed with aluminum chips	6	11.0	5.0	4.2	0.001	0.002	3.74	0.24	0.06	0.002
Robena - mixed with aluminum chips	6	11.0	5.0	3.8	< 0.001	0.002	2.02	0.52	0	0.003
Maple Creek - mixed with aluminum chips	6	13.4	5.0	5.1	0.006	0.008	1.18	0.16	0.03	0.002
Valley Camp No. 3 - mixed with aluminum chips	6	7.8	5.0	6.4	< 0.001	0.001	1.03	0.32	0.53	0.003
Kraft Coarse - mixed with aluminum chips	6	29.2	5.0	5.2	0.012	0.014	0.45	0.22	0.03	0.001
Experiment No. 18a: Continuation of Experiment No. 18										
Valley Camp No. 1 - mixed with aluminum chips	7	11.0	5.0	6.6	< 0.001	< 0.001	2.12	0.25	0.23	< 0.001
Robena - mixed with aluminum chips	7	11.0	5.0	7.0	Nil	< 0.001	2.15	0.15	0.36	< 0.001
Maple Creek - mixed with aluminum chips	7	13.4	5.0	7.0	Nil	< 0.001	1.08	0.09	0.25	< 0.001
Valley Camp No. 3 - mixed with aluminum chips	7	7.8	5.0	5.9	< 0.001	0.001	1.14	0.16	0.16	0.002
Kraft Coarse - mixed with aluminum chips	7	29.2	5.0	4.1	< 0.001	< 0.001	0.35	0.19	0	0.002
Experiment No. 18b: Continuation of Experiment Nos. 18 and 18a, samples flushed with 200 ml of electrolyte after 6 days exposure to moist air										
Valley Camp No. 1 - mixed with aluminum chips	6	11.0	5.0	6.7	< 0.001	< 0.001	0.80	0.15	0.07	0.001
Robena - mixed with aluminum chips	6	11.0	5.0	6.9	< 0.001	< 0.001	0.81	0.08	0.21	< 0.001
Maple Creek - mixed with aluminum chips	6	13.4	5.0	7.3	Nil	< 0.001	0.52	0.09	0.29	0.002
Valley Camp No. 3 - mixed with aluminum chips	6	7.8	5.0	7.2	Nil	< 0.001	0.47	0.10	0.52	0.002
Kraft Coarse - mixed with aluminum chips	6	29.2	5.0	6.0	< 0.001	< 0.001	0.15	0.08	0.03	0.002

Pyrite	Reaction time (days)	Pyrite (g)	Inhibitor (g)	pH	Iron II (mg/g)	Total iron (mg/g)	Sulfate (mg/g)	Acidity (mg $CaCO_3$/g)	Alkalinity (mg $CaCO_3$/g)	Aluminum (mg/g)
Experiment No. 19: Valley Camp No. 1 pyrite washed with electrolyte, washed pyrite mixed with alkaline candidate inhibiting agents, leached with 50 ml electrolyte daily, composite leachate analyzed										
Valley Camp No. 1 - blast furnace slag	6	11.0	5.0	6.5	< 0.001	< 0.001	2.90	0.28	0.25	
Valley Camp No. 1 - flue gas desulfurization solids	6	11.0	5.0	7.5	< 0.001	0.001	12.54	0.26	1.15	
Valley Camp No. 1 - fly ash	6	11.0	5.0	11.5	0.003	0.004	5.24	0	3.28	
Valley Camp No. 1 - neutralized acid mine drainage solids	6	11.0	5.0	7.4	< 0.001	0.002	5.94	0.14	0.32	
Valley Camp No. 1 - cement kiln dust	6	11.0	5.0	12.5	0.001[a]	Nil	6.35	0	24.22	
Experiment No. 19a: Continuation of Experiment No. 19, all samples leached with 200 ml of electrolyte following 6 days exposure to moist air										
Valley Camp No. 1 - blast furnace slag	6	11.0	5.0	6.0	< 0.001	0.001	1.22	0.17	0.10	
Valley Camp No. 1 - flue gas desulfurization solids	6	11.0	5.0	7.7	Nil	< 0.001	1.16	0.18	0.57	
Valley Camp No. 1 - fly ash	6	11.0	5.0	9.5	< 0.001	< 0.001	1.16	0	1.71	
Valley Camp No. 1 - neutralized acid mine drainage solids	6	11.0	5.0	8.5	Nil	0.001	2.01	0.13	0.77	
Valley Camp No. 1 - cement kiln dust	6	11.0	5.0	12.3	0.001	0.003	Nil[a]	0	14.72	
Experiment No. 20: Pyrite mixed with iron filings, moist air passed through mixture, washed daily with 50 ml of electrolyte (100 mg/ℓ $NaNO_3$, 100 mg/ℓ $CaCl_2$), leachate composited and analyzed										
Valley Camp No. 1 - control	6	14	0	4.0	0.006	0.004	3.94	0.27	0	
Valley Camp No. 1 - 2 parts pyrite to 1 part iron filings	6	14	7	5.1	0.058	0.087	3.40	1.75	0	
Valley Camp No. 1 - 5 parts pyrite to 1 part iron filings	6	14	2.8	5.2	0.061	0.089	2.93	1.84	0	
Valley Camp No. 1 - 10 parts pyrite to 1 part iron filings	6	14	1.4	5.4	0.068	0.094	2.81	1.14	0	
Robena - control	6	14	0	6.1	< 0.001	0.001	1.81	0.40	0.10	
Robena - 2 parts pyrite to 1 part iron filings	6	14	7	7.1	Nil	< 0.001	0.81	0.13	0.21	
Robena - 5 parts pyrite to 1 part iron filings	6	14	2.8	5.6	0.016	0.021	0.71	0.25	0.10	
Robena - 10 parts pyrite to 1 part iron filings	6	14	1.4	6.8	< 0.001	< 0.001	0.88	0.13	0.15	

Pyrite	Reaction time (days)	Pyrite (g)	Inhibitor (g)	pH	Iron II (mg/g)	Total Iron (mg/g)	Sulfate (mg/g)	Acidity (mg $CaCO_3$/g)	Alkalinity (mg $CaCO_3$/g)	Aluminum (mg/g)
Experiment No. 20a: Continuation of Experiment No. 20										
Valley Camp No. 1 - control	6	14	0	5.3	0.002	0.004	1.86	0.16	0.03	
Valley Camp No. 1 - 2 parts pyrite to 1 part iron filings	6	14	7	6.9	< 0.001	0.003	0.24	0.26	0.18	
Valley Camp No. 1 - 5 parts pyrite to 1 part iron filings	6	14	2.8	6.3	0.015	0.025	0.43	0.26	0.08	
Valley Camp No. 1 - 10 parts pyrite to 1 part iron filings	6	14	1.4	5.9	0.034	0.049	0.88	0.36	0.10	
Robena - control	6	14	0	7.1	Nil	< 0.001	1.95	0.08	0.18	
Robena - 2 parts pyrite to 1 part iron filings	6	14	7	8.6	Nil	0.004	0.18	0.05	0.31	
Robena - 5 parts pyrite to 1 part iron filings	6	14	2.8	7.5	Nil	< 0.001	0.56	0.10	0.21	
Robena - 10 parts pyrite to 1 part iron filings	6	14	1.4	7.6	Nil	< 0.001	1.11	0.11	0.27	
Experiment No. 21: Pyrite mixed with aluminum chips, moist air passed through mixture, washed daily with 50 ml electrolyte, leachate composited and analyzed										
Valley Camp No. 1 - control	6	14	0	4.0	0.006	0.004	3.94	0.27	0	-
Valley Camp No. 1 - 2 parts pyrite to 1 part aluminum chips	6	14	7	3.8	0.003	0.006	3.18	0.39	0	0.003
Valley Camp No. 1 - 5 parts pyrite to 1 part aluminum chips	6	14	2.8	3.9	0.005	0.010	3.73	0.55	0	0.004
Valley Camp No. 1 - 10 parts pyrite to 1 part aluminum chips	6	14	1.4	3.7	0.008	0.016	4.05	0.59	0	0.001
Robena - control	6	14	0	6.3	< 0.001	0.001	1.81	0.40	0.10	-
Robena - 2 parts pyrite to 1 part aluminum chips	6	14	7	4.3	0.006	0.002	1.43	0.25	0.06	0.003
Robena - 5 parts pyrite to 1 part aluminum chips	6	14	2.8	4.2	0.001	0.002	1.61	0.19	0	0.006
Robena - 10 parts pyrite to 1 part aluminum chips	6	14	1.4	2.8	0.002	0.003	1.82	0.42	0	< 0.010
Experiment No. 21a: Continuation of Experiment No. 21										
Valley Camp No. 1 - control	6	14	0	5.3	0.002	0.004	1.86	0.16	0.01	-
Valley Camp No. 1 - 2 parts pyrite to 1 part aluminum chips	6	14	7	4.5	0.003	0.004	1.83	0.33	0	0.004
Valley Camp No. 1 - 5 parts pyrite to 1 part aluminum chips	6	14	2.8	4.4	< 0.001	0.006	1.68	0.30	0	0.001
Valley Camp No. 1 - 10 parts pyrite to 1 part aluminum chips	6	14	1.4	5.9	< 0.001	< 0.001	2.02	0.19	0.06	0.001

Pyrite	Reaction time (days)	Pyrite (g)	Inhibitor (g)	pH	Iron II (mg/g)	Total Iron (mg/g)	Sulfate (mg/g)	Acidity (mg $CaCO_3$/g)	Alkalinity (mg $CaCO_3$/g)	Aluminum (mg/g)
Experiment No. 21a - Continued										
Robena - control	6	14	0	7.1	Nil	< 0.001	1.95	0.08	0.18	-
Robena - 2 parts pyrite to 1 part aluminum chips	6	14	7	6.5	< 0.001	0.006	1.00	0.09	0.12	< 0.001
Robena - 5 parts pyrite to 1 part aluminum chips	6	14	2.8	6.9	< 0.001	0.003	1.28	0.15	0.18	< 0.001
Robena - 10 parts pyrite to 1 part aluminum chips	6	14	1.4	7.0	Nil	0.006	1.51	0.10	0.25	0.001
Experiment No. 21b: Continuation of Experiment No. 21, long-term exposure to air without leaching										
Valley Camp No. 1 - control[b/]	-	-	-	-	-	-	-	-	-	-
Valley Camp No. 1 - 2 parts pyrite to 1 part aluminum fillings	12	14	0	4.5	0.009	0.011	2.29	0.93	0	0.026
Valley Camp No. 1 - 5 parts pyrite to 1 part aluminum fillings	12	14	2.8	4.7	0.007	0.009	2.79	0.55	0	0.016
Valley Camp No. 1 - 10 parts pyrite to 1 part aluminum fillings	12	14	1.4	4.8	0.005	0.006	2.84	0.42	0	0.008
Robena - control[b/]	-	-	-	-	-	-	-	-	-	-
Robena - 2 parts pyrite to 1 part aluminum fillings	12	14	7.0	7.0	< 0.001	< 0.001	0.81	0.12	0.31	0.002
Robena - 5 parts pyrite to 1 part aluminum fillings	12	14	2.8	7.1	< 0.001	< 0.001	1.84	0.18	0.25	0.002
Robena - 10 parts pyrite to 1 part aluminum fillings	12	14	1.4	7.4	0.000	0.002	2.17	0.12	0.25	0.001

a/

b/ No long-term data with control pyrites.

APPENDIX B

EXPERIMENTAL DATA: VALLEY CAMP NO. 1 PYRITE

Valley Camp No. 1--Iron II (mg/kg)

Week	Control	Nails	Fly Ash	Slag	Cement	Kiln Dust
1	5.47[a]	0.01[a]				
2	11.2[a]	0.01[a]				
3	4.95[a]	0.01[a]				
4	4.65[a]	1.83[a]				
5	9.04[a]	1.83[a]				
6	98.8[a]	45.8[a]				
7	83.8[a]	65.6[a]				
8	25.8[a]	96.3[a]				
9	63.7	95.0				
10	97.4	103				
11	153	88.4				
12	94.7	116				
13	30.3	119				10 cm column
14	20.0[a]	24.1[a]	0.01[a]	0.01[a]		5 cm column
15	4.1[a]	10.6[a]	0.01[a]	0.01[a]		
16	6.2	4.1	0.01[a]	0.01[a]		
17	79	111	0.01[a]	0.01[a]		
18	112	126	0.18[a]	0.27[a]		
19	3.36	2.48	0.04	< 0.01		
20	3.64	3.16	0.11	0.01		
21	3.61	16.0	0.21	0.01		
22	3.25	2.89	0.11	< 0.01		
23	14.1	83.1	0.16	0.09		
24	2.87	52.3	0.22	< 0.01		
25	2.68	9.37	0.15	< 0.01		
26	26.5	3.89	0.16	< 0.01		
27	31.6	7.74	0.30	0.01		
28	2.32	21.8	0.10	< 0.01	0.09[a]	0.56[a]
29	8.08	4.30	0.08	< 0.01	0.02	< 0.01
30	8.41	29.5	0.24	0.01	0.10	0.05
31	2.43	11.0	0.11	0.01	0.02	0.11
32	1.96	0.79	0.10	< 0.01	0.04	0.06
33	2.57	0.95	0.30	0.01	< 0.01	0.02
34	2.41	1.13	0.10	< 0.01	0.02	< 0.01
35	1.49	1.08	0.34	< 0.01	0.02	< 0.01
36	1.64	3.44	0.10	< 0.01	0.02	0.02
37	1.49	1.36	0.14	< 0.01	< 0.01	< 0.01
38	1.46	1.01	0.15	0.01	0.02	< 0.01

[a] Data not used in statistical analysis. System reaching steady-state equlibrium.

Valley Camp No. 1--iron total (mg/kg)

Week	Control	Nails	Fly Ash	Slag	Cement	Kiln Dust
1	10.0[a]	0.09[a]				
2	22.2[a]	0.26[a]				
3	20.7[a]	0.17[a]				
4	12.2[a]	3.23[a]				
5	33.5[a]	19.5[a]				
6	125[a]	49.3[a]				
7	242[a]	70.3[a]				
8	434[a]	103[a]				
9	468	133				
10	505	168				
11	382	165				
12	379	227				
13	454	260				10 cm column
14	60.0[a]	32.2[a]	0.01[a]	0.03[a]		5 cm column
15	226[a]	174[a]	0.18[a]	0.04[a]		
16	331	238[a]	0.30[a]	0.05[a]		
17	741	405[a]	0.66[a]	0.03[a]		
18	400	280	1.34	0.67		
19	277	269	0.82	0.22		
20	394	327	1.51	0.21		
21	392	394	8.86	1.83		
22	366	362	1.55	0.50		
23	296	316	2.32	0.12		
24	239	406	1.58	0.14		
25	258	342	2.97	0.09		
26	312	413	4.68	0.05		
27	272	290	6.43	0.08		
28	208	247	5.01	0.06	4.80[a]	1.20[a]
29	216	206	1.86	0.04	0.10	0.13
30	263	261	2.68	0.08	0.29	1.39
31	210	74.2	2.07	0.04	1.63	0.15
32	200	113	4.35	0.04	0.42	0.13
33	208	118	5.49	0.03	0.53	0.17
34	231	113	5.87	0.03	0.31	0.15
35	181	123	6.31	0.12	0.78	0.15
36	153	124	5.75	0.32	0.24	0.15
37	138	96.3	5.29	0.04	0.92	0.22
38	127	70.3	5.66	0.05	0.97	0.14

a/ Data not used in statistical analysis. System reaching steady-state equilibrium.

Valley Camp No. 1--sulfate (mg/kg)

Week	Control	Nails	Fly Ash	Slag	Cement	Kiln Dust
1	367[a]	194[a]				
2	400[a]	243[a]				
3	383[a]	259[a]				
4	518[a]	340[a]				
5	614[a]	354[a]				
6	878[a]	528[a]				
7	1,490[a]	613[a]				
8	1,730	595				
9	1,872	609				
10	1,872	797				
11	1,492	763				
12	1,420	961				
13	1,818	1,062				10 cm column
14	554[a]	349[a]	2,176[a]	571[a]		5 cm column
15	1,171[a]	785[a]	3,967[a]	454[a]		
16	1,756	1,157	2,426[a]	402[a]		
17	1,629	1,173	981[a]	340[a]		
18	1,260	1,006	714[a]	325[a]		
19	1,048	888	725	653		
20	1,294	1,055	725	352		
21	1,357	1,109	506	325		
22	1,362	1,074	393	284		
23	937	584	353	280		
24	860	616	346	324		
25	1,013	649	396	360		
26	1,380	710	468	352		
27	1,147	967	470	360		
28	870	949	459	342	305[a]	254[a]
29	904	752	343	299	90	899
30	899	865	187	298	57	608
31	760	352	369	305	44	513
32	748	649	369	264	35	388
33	831	662	452	333	38	271
34	845	643	367	382	33	191
35	761	613	368	359	37	118
36	777	707	390	356	34	112
37	645	521	354	410	31	88
38	566	419	455	312	37	94

[a] Data not used in statistical analysis. System reaching steady-state equilibrium.

Valley Camp No. 1--acidity (mg $CaCO_3$/kg)

Week	Control	Nails	Fly Ash	Slag	Cement	Kiln Dust
1	55[a]	4.9[a]				
2	96[a]	8.7[a]				
3	96[a]	2.8[a]				
4	190[a]	16[a]				
5	518[a]	74[a]				
6	887[a]	160[a]				
7	1,177[a]	245[a]				
8	1,550[a]	242[a]				
9	1,910	330				
10	1,910	561				
11	1,492	638				
12	1,363	814				
13	1,685	931				10 cm column
14	237[a]	135[a]	8.9[a]	3.9[a]		5 cm column
15	906[a]	545[a]	38[a]	4.1[a]		
16	1,580	1,002	32[a]	3.2[a]		
17	1,378	1,045	18[a]	3.0[a]		
18	1,070	822	28[a]	6.1[a]		
19	989	785	32	3.6		
20	1,264	1,044	72	4.3		
21	1,113	970	41	3.9		
22	1,159	1,033	36	3.0		
23	880	841	23	6.6		
24	650	691	27	4.3		
25	755	631	70	5.2		
26	1,011	749	154	3.8		
27	821	687	196	5.5		
28	629	673	161	5.9	3.7[a]	1.5[a]
29	731	537	83	4.6	0	0
30	698	531	86	3.9	0	0
31	663	154	91	4.4	0	0
32	463	364	113	3.9	0	0
33	643	406	110	5.9	0	0
34	644	416	98	6.6	0	0
35	548	315	98	5.0	0	0
36	552	449	88	4.9	0	0
37	514	337	87	4.7	0	0
38	497	284	89	2.6	0	0

[a] Data not used in statistical analysis. System reaching steady-state equilibrium.

Valley Camp No. 1--alkalinity (mg $CaCO_3$/kg)

Week	Control	Nails	Fly Ash	Slag	Cement	Kiln Dust
1	0.5[a]	22[a]				
2	2.3[a]	19[a]				
3	3.2[a]	12[a]				
4	0[a]	3.6[a]				
5	0[a]	0[a]				
6	0[a]	0[a]				
7	0[a]	0[a]				
8	0[a]	0[a]				
9	0	0				
10	0	0				
11	0	0				
12	0	0				
13	0	0				10 cm column
14	0[a]	0[a]	9.9[a]	1.6[a]		5 cm column
15	0[a]	0[a]	14[a]	5.8[a]		
16	0	0	4.0[a]	5.6[a]		
17	0	0	12[a]	11[a]		
18	0	0	5.0[a]	13[a]		
19	0	0	2.1	15		
20	0	0	6.4	19		
21	0	0	0	21		
22	0	0	0	24		
23	0	0	0	27		
24	0	0	0	23		
25	0	0	0	31		
26	0	0	0	19		
27	0	0	0	18		
28	0	0	0	17	9.6[a]	8.9[a]
29	0	0	0	8.8	74	262
30	0	0	0	26	109	335
31	0	0	0	21	113	333
32	0	0	[illegible]	23	105	279
33	0	0	0	24	157	273
34	0	0	0	20	115	214
35	0	0	0	22	117	190
36	0	0	0	24	123	187
37	0	0	0	26	114	157
38	0	0	0	13	121	143

[a] Data not used in statistical analysis. System reaching steady-state equilibrium.

Valley Camp No. 1--pH

Week	Control	Nails	Fly Ash	Slag	Cement	Kiln Dust
1	5.4[a]	7.7[a]				
2	4.7[a]	7.8[a]				
3	4.7[a]	7.6[a]				
4	3.8[a]	6.3[a]				
5	3.2[a]	5.3[a]				
6	3.3[a]	4.3[a]				
7	3.1[a]	4.0[a]				
8	2.7[a]	3.5[a]				
9	2.5	3.2				
10	2.6	2.9				
11	2.5	2.8				
12	2.4	2.6				
13	2.2	2.5				10 cm column
14	2.5[a]	2.7[a]	7.0[a]	6.3[a]		5 cm column
15	2.3[a]	2.5[a]	6.4[a]	5.8[a]		
16	2.3	2.4	6.2[a]	6.0[a]		
17	2.2	2.4	6.0[a]	6.0[a]		
18	2.4	2.5	5.8[a]	6.1[a]		
19	2.3	2.5	6.0	6.8		
20	2.3	2.5	4.5	7.4		
21	2.3	2.5	3.3	7.3		
22	2.2	2.4	3.2	7.1		
23	2.6	2.8	4.0	7.1		
24	2.6	2.7	3.5	6.9		
25	2.3	2.5	3.0	6.8		
26	2.1	2.2	2.6	7.0		
27	2.2	2.3	2.6	6.4		
28	2.3	2.5	2.7	6.8	6.3[a]	8.9[a]
29	2.9	3.0	2.7	6.0	10.5	12.3
30	3.0	3.2	3.2	6.3	10.6	12.5
31	2.2	2.3	2.5	7.1	10.8	11.9
32	2.0	2.2	2.6	7.5	10.8	11.7
33	2.3	2.5	2.8	7.8	11.1	11.9
34	2.2	2.4	2.7	7.2	11.0	11.7
35	2.3	2.5	2.7	7.0	10.8	11.6
36	2.3	2.5	2.8	6.9	10.9	11.5
37	2.4	2.6	3.0	7.4	11.0	11.6
38	2.2	2.4	2.7	6.5	10.7	11.2

[a] Data not used in statistical analysis. System reaching steady-state equilibrium.

APPENDIX C

EXPERIMENTAL DATA: ROBENA AND MAPLE CREEK PYRITES

Robena and Maple Creek Iron II (mg/kg)

Week	Control	Nails	Fly Ash	Slag
Robena (10 cm column)				
1	0.02	< 0.01		
2	< 0.01	< 0.01		
3	< 0.01	< 0.01		
4	0.01	< 0.01		
5	< 0.01	< 0.01		
6	0.02	< 0.01		
7	< 0.01	< 0.01		
8	< 0.01	< 0.01		
9	< 0.01	< 0.01		
10	0.03	< 0.01		
11	0.02	< 0.01		
12	0.02	0.03		
13	0.01	< 0.01		
Maple Creek (5 cm column)				
1[a/]	17	63	14	31
2[a/]	12	45	0.57	26
3	0.04	13	0.04	2.2
4	0.05	9.7	0.01	1.2
5	0.02	6.4	< 0.01	0.22
6	< 0.01	3.2	< 0.01	0.05
7	0.01	4.0	< 0.01	< 0.01
8	0.01	4.4	0.01	0.02
9	< 0.01	0.11	< 0.01	0.02
10	0.02	< 0.01	< 0.01	0.13
11	0.01	0.01	< 0.01	< 0.01
12	0.01	0.02	0.01	0.04
13	0.01	< 0.01	< 0.01	0.01
14	< 0.01	< 0.01	< 0.01	0.01
15	0.01			0.02
16	0.02			< 0.01
17	0.02			0.03
18	0.02			< 0.01
19	0.01			0.01
20	< 0.01			0.03
21	0.02			< 0.01
22	0.01			< 0.01
23	0.01			0.01
24	0.01			0.01
25	0.02			0.02

a/ Data not used in statistical analysis. System reaching steady-state equilibrium.

Robena and Maple Creek iron total (mg/kg)

Week	Control	Nails	Fly Ash	Slag
Robena (10 cm column)				
1	0.06	0.17		
2	0.05	0.10		
3	0.07	0.07		
4	0.04	0.02		
5	0.09	0.02		
6	0.20	0.01		
7	0.23	0.01		
8	0.10	0.03		
9	0.11	0.01		
10	2.5	0.02		
11	0.26	0.01		
12	0.17	0.02		
13	0.05	0.08		
Maple Creek (5 cm column)				
1[a/]	18	66	16	34
2[a/]	18	53	0.98	36
3	0.27	14	0.24	3.1
4	1.9	10	0.04	2.4
5	3.8	6.4	0.03	0.32
6	0.18	3.8	0.05	0.73
7	0.11	4.9	0.04	0.03
8	0.22	4.9	0.05	0.38
9	0.04	0.94	0.05	0.20
10	0.13	0.55	0.10	0.77
11	0.14	0.15	0.04	0.59
12	0.12	0.09	0.05	1.6
13	0.11	0.10	0.07	0.10
14	0.09	1.2	0.04	0.05
15	0.04			0.07
16	0.07			0.25
17	0.09			0.27
18	0.05			0.47
19	0.06			0.78
20	0.09			1.3
21	1.2			1.6
22	1.1			2.4
23	0.21			1.6
24	0.05			0.24
25	0.07			0.67

a/ Data not used in statistical analysis. System reaching steady-state equilibrium.

Robena and Maple Creek sulfate (mg/kg)

Week	Control	Nails	Fly Ash	Slag
Robena (10 cm column)				
1	200	209		
2	329	261		
3	203	197		
4	336	364		
5	324	284		
6	356	334		
7	320	372		
8	364	348		
9	301	302		
10	334	306		
11	317	290		
12	340	389		
13	292	369		
Maple Creek (5 cm column)				
1[a/]	337	523	841	280
2[a/]	1,102	1,288	6,491	1,364
3	675	714	2,357	827
4	919	823	827	971
5	464	440	1,100	463
6	418	359	564	376
7	317	246	490	361
8	260	224	422	324
9	227	212	376	307
10	212	163	344	242
11	199	263	372	297
12	265	250	322	292
13	250	242	325	274
14	236	234	328	262
15	237			320
16	230			300
17	202			234
18	261			294
19	237			298
20	272			260
21	272			271
22	277			277
23	305			271
24	281			248
25	253			333

a/ Data not used in statistical analysis. System reaching steady-state equilibrium.

Robena and Maple Creek acidity (mg $CaCO_3$/kg)

Week	Control	Nails	Fly Ash	Slag
Robena (10 cm column)				
1	4.8	5.0		
2	4.8	5.8		
3	5.0	0.8		
4	7.8	12		
5	5.0	18		
6	3.9	20		
7	5.8	24		
8	5.1	26		
9	4.4	23		
10	8.9	24		
11	4.8	29		
12	4.3	36		
13	30	3.7		
Maple Creek (5 cm column)				
1[a/]	75	161	68	77
2[a/]	41	96	21	74
3	5.5	40	16	13
4	7.5	34	17	4.4
5	8.0	25	18	8.2
6	2.5	11	7.9	3.8
7	3.2	12	7.8	5.8
8	5.4	17	8.0	4.8
9	1.6	3.0	6.4	5.2
10	3.5	1.7	6.7	7.0
11	4.4	1.8	4.4	6.7
12	7.2	1.9	6.4	9.7
13	4.2	2.2	5.4	6.1
14	4.8	3.6	4.7	8.3
15	6.3			7.9
16	5.3			6.2
17	2.6			4.5
18	2.7			1.5
19	2.8			4.3
20	2.1			4.9
21	5.5			5.0
22	3.2			4.4
23	6.2			5.8
24	4.5			2.6
25	3.2			3.6

a/ Data not used in statistical analysis. System reaching steady-state equilibrium

Robena and Maple Creek--alkalinity (mg $CaCO_3$/kg)

Week	Control	Nails	Fly Ash	Slag
Robena (10 cm column)				
1	26	28		
2	33	37		
3	24	30		
4	36	40		
5	27	28		
6	21	25		
7	29	20		
8	22	18		
9	17	20		
10	19	18		
11	17	18		
12	20	23		
13	6.6	25		
Maple Creek (5 cm column)				
1[a/]	0	0	0	0
2[a/]	24	11	49	0
3	32	13	30	2.6
4	30	14	27	16
5	28	8.8	23	25
6	27	2.1	24	16
7	28	2.1	24	20
8	30	0	24	17
9	28	1.3	23	19
10	31	8.6	22	24
11	25	7.0	27	24
12	40	8.3	30	42
13	34	12	30	32
14	41	12	30	29
15	19			14
16	19			12
17	37			21
18	20			33
19	36			15
20	33			12
21	24			16
22	14			29
23	26			8.5
24	25			12
25	13			27

a/ Data not used in statistical analysis. System reaching steady-state equlibrium.

Robena and Maple Creek--pH

Week	Control	Nails	Fly Ash	Slag
Robena (10 cm column)				
1	8.1	8.1		
2	8.2	8.2		
3	8.5	8.5		
4	8.2	8.1		
5	6.1	7.0		
6	6.7	6.8		
7	6.3	6.2		
8	6.1	6.1		
9	7.6	6.8		
10	6.1	6.1		
11	6.5	6.5		
12	6.8	6.1		
13	6.1	7.6		
Maple Creek (5 cm column)				
1[a/]	3.5	3.3	3.4	4.4
2[a/]	5.9	5.8	6.5	3.6
3	6.3	6.1	6.3	4.9
4	6.3	6.0	6.9	6.1
5	6.4	5.9	6.4	6.0
6	7.1	6.4	7.5	6.0
7	7.5	5.4	7.8	6.4
8	7.3	5.8	7.8	6.3
9	7.9	7.7	7.9	7.6
10	7.5	7.8	7.7	6.6
11	7.0	7.1	7.8	6.6
12	7.2	7.2	7.9	7.4
13	6.9	6.9	7.5	6.6
14	7.0	7.1	7.6	6.6
15	7.5			6.8
16	5.6			5.5
17	6.7			5.7
18	7.4			7.4
19	7.6			6.5
20	7.2			6.3
21	6.4			5.9
22	6.8			5.9
23	6.5			5.8
24	6.4			5.7
25	6.5			6.2

a/ Data not used in statistical analysis. System reaching steady-state equilibrium.